QUANTA CHEMISTRY CLASSES
An institute of Chemical Sciences

1

ATOMIC STRUCTURE AND QUANTUM

HINTS & SOLUTIONS

GATE 2005

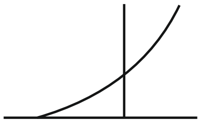
1. The set of eigen function is $\sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$ is normalized.

$$\int_0^a \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} dx = \rightarrow \text{normalized if } n = 1$$

$$\int_0^a \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a} \sqrt{\frac{2}{a}} \sin \frac{2\pi x}{a} dx = 0 \rightarrow = \text{orthogonal}$$

Correct option is (c)

2. eax^2 $(\alpha > 0)$

(1) Continuous  (2) $\left| e^{ax^2} \right|_{x = \infty} = e^{\infty} = \infty$

$$\int_{-\infty}^{+\infty} e^{\alpha x^2} e^{\alpha x^2} dx = \infty$$

It is not normalized

Correct option is (c)

3. $$\psi = \int_{-\infty}^{+\infty} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2x}} x^3 \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\frac{\beta x^2}{2}} dx \Rightarrow \left(\frac{\beta}{\pi}\right)^{1/2} \int_{-\infty}^{+\infty} x^3 e^{-\beta x^2}$$

$x^n = n = \text{even},$ $\Psi \neq 0$

$x^n = n = \text{odd},$ $\Psi \neq 0$

$\Delta\varepsilon_n^{(1)} = 0$

Correct option is (d)

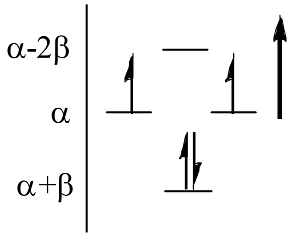
4. $$\psi_{2s} = \psi_{200} = \frac{1}{4\sqrt{2\pi}} a_0^{3/2}\left(q - \frac{r}{a_0}\right)e^{-r/2a_0}$$

For radial noe total function = 0

$$\frac{1}{4\sqrt{2\pi}} a_0^{3/2}\left(q - \frac{r}{a_0}\right)e^{-\frac{-r}{2a_0}} = 0 \Rightarrow \left(q - \frac{r}{q_0}\right) = 0 \Rightarrow r = 2a_0$$

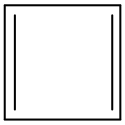
Correct option is (c)

5.(5,6) (a)

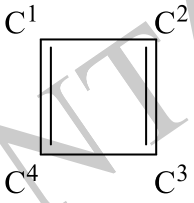


$(\alpha - 2\beta) - \alpha = -2\beta = -2 \times 75$ kJ/mole = 150 kJ

Correct option is (a)

(b) **Cyclobutadiene**  :

Matrix → [4 × 4]



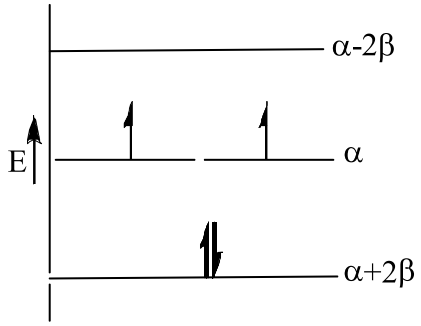
$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} \\ C_{21} & C_{22} & C_{23} & C_{24} \\ C_{31} & C_{32} & C_{33} & C_{34} \\ C_{41} & C_{42} & C_{43} & C_{44} \end{bmatrix} \Rightarrow \begin{bmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{bmatrix}$$

$$\Rightarrow \begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0 \quad \left(\because x = \frac{\alpha - E}{\beta}\right)$$

$\Rightarrow$ $x[x(x^2 - 1) - 1(x - 0) - 1] - 1[1(x^2 - 1) - 1(0 - 1)] - 1[1(1 - 0) - x(0 - x) + 1(0 - 1)] = 0$

$\Rightarrow$ $x[x^3 - x - x] - 1[x^2 - 1 + 1] - [1 + x^2 - 1] = 0 \Rightarrow x^4 - 2x^2 - x^2 - x^2 = 0$

$\Rightarrow$ $x^4 - 4x^2 = 0$



$\Rightarrow\ x^2(x+2)(x-2)=0;$

$\therefore\ x = 0, x = 0$ (two energy level) and $x = +2, x = -2$

$E_1 = \alpha + 2\beta;\ E_2 = \alpha,\ E_3 = \alpha,\ E_4 = \alpha - 2\beta$

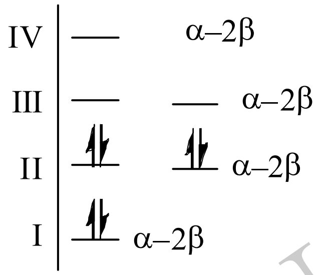
Linked Answer Q. 5 (a) and Q. 6 (b):

7. The orbital $\psi = Is_{H_A} - Is_{H_B}$ of water belongs to B_1 irreducible representation

Correct option is (b)

GATE 2006

8.



Transition from I to IV ⇒ |–4β|; Transition from I to III ⇒ |–3β|

Transition from II to III ⇒ |–2β|; Transition from II to IV ⇒ |–3β|

So, β is not occur in upper transition

Correct option is (d)

9.
$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix}$$

$$H_{11} = \left\langle \Psi_{2s} + \Psi_{3s} \left| H \right| \Psi_{2s} + \Psi_{3s} \right\rangle = -\frac{13.6}{4} - \frac{13.6}{9}$$

$$H_{22} = \left\langle \Psi_{2s} - \Psi_{3s} \left| H \right| \Psi_{2s} - \Psi_{3s} \right\rangle = -\frac{13.6}{4} - \frac{13.6}{9}$$

$$H_{12} = H_{21} = \left\langle \Psi_{2s} - \Psi_{3s} \left| H \right| \Psi_{2s} + \Psi_{3s} \right\rangle = -\frac{13.6}{4} - \frac{13.6}{9}$$

$$S_{21} = S_{12} = \left\langle \Psi_{2s} + \Psi_{3s} \mid \Psi_{2s} - \Psi_{3s} \right\rangle = 1 - 1 = 0;\ S_{11} = \left\langle \Psi_{2s} + \Psi_{3s} \mid \Psi_{2s} - \Psi_{3s} \right\rangle = 1 + 1 = 2$$

$$S_{22} = \left\langle \Psi_{2s} + \Psi_{3s} \mid \Psi_{2s} - \Psi_{3s} \right\rangle = 1 + 1 = 2$$

$$\begin{vmatrix} 3.4(1+4)2-E & 3.4(1-4/9)/2 \\ 3.4(1-4/9)/2 & 3.4(1+4/9)2-E \end{vmatrix}$$

Correct option is (a)

10. $$\left[\frac{d}{dx}, \frac{d^2}{dx^2}+2\frac{d}{dx}\right]\Psi \Rightarrow \frac{d}{dx}\left(\frac{d^2}{dx^2}+2\frac{d}{dx}\right)\Psi - \left(\frac{d^2}{dx^2}+\frac{2d}{dx}\right)\frac{d}{dx}\Psi$$

$$\Rightarrow \frac{d}{dx}\left(\frac{d^2\Psi}{dx^2}+2\frac{d\Psi}{dx}\right)-\left(\frac{d^2}{dx^2}+\frac{2d}{dx}\right)\frac{d\Psi}{dx};\frac{d^3\Psi}{dx^3}+2\frac{d^3\Psi}{dx^3}-2\frac{d^2\Psi}{dx^2}=0$$

Commute each other.

11. For a particle in a box from –a to + a,

Wave function is

$$\Psi_n(x)=\sqrt{\frac{1}{a}}\sin\left(\frac{n\pi x}{2a}\right)$$

For the excited state, n = 2. Then

$$\boxed{\Psi=\sqrt{\frac{1}{a}}\sin\left(\frac{\pi x}{a}\right)}$$

Correct option is (b)

12. $$\int_{-a}^{a}\sqrt{\frac{1}{a}}\sin\frac{\pi x}{a}\,\delta(x-a/2)\sqrt{\frac{1}{a}}\sin\frac{\pi x}{a}dx$$

From dirac-delta property

$$x-\frac{a}{2}=0\Rightarrow x=\frac{a}{2}$$

x lie under limit

So, not need to solve integrity,

$$\sqrt{\frac{1}{a}}\sin\frac{\pi a}{a^2}\sqrt{\frac{1}{a}}\sin\frac{\pi a}{a^2}=\frac{1}{a}\times 1\times 1=\frac{1}{a}$$

Correct option is (c)

GATE 2007

13. $E = h\nu$

$$h=\frac{E}{\nu}=\frac{J}{s^{-1}}$$

E or ω = force × distance

= mass × acceleration × distance

= $kg \times ms^{-2} \times m$

$$\text{Unit of h} = \frac{\text{kg m}^2\text{s}^{-2}}{\text{s}^{-1}} = \text{kgm}^2\ \text{s}^{-1}$$

Dimension of h is ML^2T^{-1}

Correct option is (b)

14. Energy order of molecular orbital be given as

$$1\sigma_g < 1\sigma_u^* < 2\sigma_g < 2\sigma_u^* < 3\sigma_g < 1(\pi_u = \pi_u) < 1\left(\pi_g^* = \pi_g^*\right) < 3\sigma_u^*$$

Correct option is (d)

15. $$\frac{13.6\times(z_{\text{eff}})^2}{n^2} = \frac{13.6\times(1.84)^2}{9} = \frac{13.6\times1.84\times1.84}{9} = 5.1\ \text{eV}$$

Correct option is (c)

16. $$\Delta E = \int_0^{2\pi} \psi_m^*\ H\psi_m\ dT = \int_0^{2\pi} \frac{1}{\sqrt{2\pi}} e^{im\phi}\rho\cos\phi \frac{1}{\sqrt{2\pi}} e^{-im\phi} d\phi = \frac{\rho}{2\pi}\int_0^{2\pi} \cos\rho d\phi = \frac{\rho}{2\pi}[\sin\phi]_0^{2\pi}$$

$$= \frac{\rho}{2\pi}[\sin 2\pi - \sin 0] = \frac{\rho}{2\pi}\ \alpha\ 0 = 0$$

Correct option is (a)

17. $$\int_0^a \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\langle Px\rangle\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{L}dx$$

$$\frac{2}{L}\int_0^a \sin\frac{\pi x}{L}\left(-i\hbar\frac{d}{dn}\right)\sin\frac{\pi n}{L}dx; \frac{2}{L}\int_0^a \sin\frac{\pi x}{L}(-\hbar) - \cos\frac{\pi n}{L}dx \times \frac{L}{\pi}dx$$

$$\frac{2}{L}(-\hbar)\left(-\frac{L}{\pi}\right)\int_0^a \sin\frac{\pi n}{L}\cos\frac{\pi n}{L}dx; \frac{1}{L}(-\hbar)\left(-\frac{L}{\pi}\right)\int_0^a 2\sin\frac{\pi n}{L}\cos\frac{\pi n}{L}dx$$

$$\frac{1}{L}(-\hbar)\left(-\frac{L}{\pi}\right)\int_0^a \sin\frac{2\pi n}{L}dx; -\frac{L}{\pi}\frac{1}{L}(-\hbar)\frac{L}{2\pi}\left[\cos\frac{2\pi n}{a}\right]_0^a = \frac{i\hbar}{2a}[\cos 2\pi - \cos 0][1-1] = 0$$

Correct option is (a)

18. $$\Delta P_x = \sqrt{\langle P_x^2\rangle - \langle P_x\rangle^2} = \sqrt{\left\langle\frac{n^2h^2}{4\ell^2}\right\rangle - \langle 0\rangle^2} = \frac{nh}{2\ell} \quad n = 1 = \frac{h}{2\ell} \quad \ell = a = \frac{h}{2a}$$

Correct option is (c)

GATE 2008

19. $\Delta t = 10^{-10}$ s

$$\Delta E \Delta t \geq \frac{\hbar}{4\pi}$$

$$\Delta E = \frac{\hbar}{4\pi \times \Delta t} = \frac{6.63 \times 10^{-34}\,\text{J.S}}{4 \times 3.14 \times 10^{-10}\,\text{S}}$$

leV = 1.6×10^{-19} J

$$= \frac{6.63 \times 10^{-34}\,\text{eV}}{4 \times 3.14 \times 10^{-10} \times 1.6 \times 10^{-19}} = \frac{6.63 \times 10^{-34}\,\text{eV}}{4 \times 3.14 \times 16}$$

$$= \frac{6.63 \times 10^{-5}}{20.096} = 0.32 \times 10^{-5}\ \text{eV} = 3.2 \times 10^{-6}\ \text{eV}$$

Correct option is (b)

20. $\psi = 0.89\psi_{\text{convalent}} + 0.45\psi_{\text{ionic}}$

Chance that both electron of the bond will be found on the same atom means ionic bond found $0.45\psi_{\text{ionic}}$

$(0.45)^2 = 20.25$

$0.2025 \times 100 = 20$

Correct option is (b)

21. Electronic energy = $-0.5n^2$

for He z = 2 = $-0.5 \times 4 = -2.0$

Correct option is (c)

22. % charge = $\left|2\frac{d\ell}{\ell}\right| \times 100 = \left|2\frac{10^{-9}\,\text{mtr}}{10^{-3}\,\text{mtr}}\right| \times 100 = 2 \times 10^{-6} \times 100 = 2 \times 10^{-4}$

Correct option is (a)

23. $$\left[x \cdot \frac{d}{dx}\right]\psi; \left[x\frac{d}{dx}\psi - \frac{d}{dx}n\psi\right]$$

$$x\frac{d\psi}{dx} - \frac{d}{dx}\overset{\text{I II}}{(n\psi)}; x\frac{d\psi}{dx} - \left(x\frac{d\psi}{dx} + \psi\frac{d}{dx}x\right)$$

$$\left[x\frac{d\psi}{dx} - x\frac{d\psi}{dx}\overset{\text{I II}}{(n\psi)}; -\psi\right]; -\psi = -1\,\psi = f(x); -f(x)$$

Correct option is (c)

24. $$\frac{\lambda}{\text{pm}} = \left(\frac{a}{\phi}\right)^{1/2}$$

$$\Rightarrow \frac{h}{\sqrt{2me\phi}\,\text{pm}} = \left(\frac{a}{\phi}\right)^{1/2} \qquad \Rightarrow a^{1/2} = \frac{h}{\sqrt{2me}\ \text{pm}}$$

$$\Rightarrow a = \frac{h^2}{2me(\text{pm})^2} = \frac{(6.6 \times 10^{-34})}{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} \times 10^{-12}\,\text{mtr} \times 10^{-12}\,\text{mtr}}$$

$$= \frac{6.6 \times 10^{-34} \times 6.6 \times 10^{-34}\,\text{J.sec} \times \text{J sec}}{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} \times 10^{-12} \times 10^{-12}} = \frac{6.6 \times 6.6}{2 \times 9.1 \times 16} \times 10^{-68} \times 10^{64}$$

$$= \frac{66\times 66}{2\times 91\times 16}\times 10^6 = \frac{4356}{2912}\times 10^6 = 1.5\times 10^6\ \text{eV}$$

Correct option is (b)

GATE 2009

25. Lowest energy equal to zero for a rigid rotor

$E = BJ(J + 1)\ J = 0,1,23 - - -$

$J = 0$

$E = B \times 0\,(0 + 1)$

$E = 0$

Correct option is (b)

26. $12h^2/8ml^2$ ———————— (222)

$11h^2/8ml^2$ ———————— $n = (311)\ (131)\ (113)$

$9h^2/8ml^2$ ———————— $n = (221)\ (122)\ (212)$

$6h^2/8ml^2$ ———————— $n = (211)\ (121)\ (112)$

$3h^2/8ml^2$ ———————— $n_x = 1,\ n_y = 1,\ n_2 = 1$

$$\text{Ground state energy} = (1\ 1\ 1) = \frac{\left(n_x^2, n_y^2, n_z^2\right)h^2}{8ml^2} = \frac{3h^2}{8ml^2}$$

$$\text{4 times energy of ground state} = \frac{4\times 3h^2}{8ml^2} = \frac{12h^2}{8ml^2} = \frac{\left(n_x^2 n_y^2 n_z^2\right)h^2}{8ml^2} = \frac{\left(2^2+2^2+2^2\right)h^2}{8ml^2}$$

$(n_x, n_y, n_z) = 2\ 2\ 2 \rightarrow$ degeneracy = 1

Correct option is (c)

27. $\lambda = \frac{h}{P};\ \lambda = \frac{h}{mv}$

$$\lambda = \frac{6.63\times 10^{-34}\ \text{J.S}}{4\times 6.023\times 10^{23}\times 1000\,\text{m/s}} \Rightarrow \lambda = \frac{6.63\times 10^{-34}}{4\times 6.023\times 10^{25}}\text{m} \Rightarrow \lambda = \frac{6.63}{24.092}$$

$$\lambda = \frac{6.63\times 10^{-34}\ \text{J.S}}{4\times 1.67\times 10^{-27}\times 1000}\ \frac{\text{kgm}}{\text{S}} = \frac{6.63\times 10^{-34}\times 10^{-24}}{4\times 1.67}$$

$$= \frac{6.63\times 10^{-10}}{6.68}\text{m} = 99.25\times 10^{-12}\ \text{mtr} = 0.99\times 10^{-10}\ \text{m}$$

Correct option is (a)

GATE 2010

28. $\psi_2 = \sqrt{\frac{2}{b}}\sin\left(\frac{2\pi x}{b}\right) \Rightarrow \int_0^b \psi_2\psi_2^* d\tau = 1$ [normalised]

$$\int \psi_2 \psi_1 d\tau = \int_0^b \sqrt{\frac{1}{b}} \sin \frac{\pi x}{b} \Rightarrow \sqrt{\frac{2}{b}} \sin \frac{2\pi x}{b} dx = 0 \qquad \text{[orthogonal]}$$

Correct option is (c)

29. $[x^3, P_x]$ $\qquad \Rightarrow [x^x, P_x] = xi\hbar x^{n-1}$

$$\Rightarrow [x^3, P_x] \qquad = 3x^2 i\hbar = \frac{3x^2 i\hbar}{2\pi} = \frac{i}{i} \times \frac{3x^2 i\hbar}{2\pi} \qquad \Rightarrow \boxed{\frac{-3x^2\hbar}{2\pi i}}$$

30. $E = h\nu$ $\qquad E = \dfrac{n^2\hbar^2}{8mb^2}$

$$E_1 = \frac{(1)^2\hbar^2}{8mb^2} \qquad E_2 = \frac{(1)^2\hbar^2}{8mb^2}$$

$$E_2 - E_1 = \frac{\hbar^2}{8mb^2}(9-1) \Rightarrow E_2 - E_1 = \frac{\hbar^2}{mb^2}$$

$$h\nu = \frac{\hbar^2}{mb^2} \qquad \Rightarrow \boxed{v = \frac{h}{mb^2}}$$

Correct option is (c)

GATE 2011

31. $\psi = N \times e^{\frac{ax^2}{2}}$

$$\frac{d\psi}{dx} = N \times e^{-ax^2/2} + N \times e^{-\frac{ax^2}{2}}(-ax) = N\, e^{-ax^2/2}[i - ax^2] \qquad \Rightarrow x = \pm \frac{1}{\sqrt{a}}$$

Further differentiation,

$$\frac{d^2\psi}{dx^2} = N \exp\left(-\frac{ax^2}{2}\right)(-2ax) + (1 - ax^2); \qquad \left[N \exp\left(-\frac{ax^2}{2}\right)\left(\frac{-2ax}{2}\right)\right]$$

$$N\, e^{-\frac{ax^2}{2}}[-2ax + (1 - x^2)(-ax)] = Ne^{-ax^2/2}[-3ax + a^2x^3]$$

$$\text{At } x = -\frac{1}{\sqrt{a}}, \qquad \frac{d^2\psi}{dx^2} = Ne^{-\frac{a\left(-1\sqrt{a}\right)^2}{2}}\left[-3a\left(-\frac{1}{\sqrt{a}}\right) + a^2\left(-\frac{1}{\sqrt{a}}\right)^3\right]$$

$$= N\,N\, e^{-½}\left(2\sqrt{a}\right) > 0 \quad \text{(minima)}$$

$$\text{At } x = +\frac{1}{\sqrt{a}}, \ \frac{d^2\psi}{dx^2} = Ne^{\left[\frac{-a\left(1/\sqrt{a}\right)^2}{2}\right]\left[-3a\left(\frac{1}{\sqrt{a}}\right) + a^2\left(\frac{-1}{\sqrt{a}}\right)^3\right]}$$

$$= N\,e^{-½\left[-3\sqrt{a}+\sqrt{a}\right]} = N\,e^{-½\left[2\sqrt{a}\right]} < 0 \quad \text{(maximum)}$$

Hence, one maxima and one minima.

Correct option is (b)

32. From variation principle, if we are used an arbitary wave function and calculate the energy of a quantum mechanical system the value calculated is never less than the true energy. This principle used for the validity of function.

$E\phi > E_0$

Where, $E\phi$ = energy calculated

E_0 = energy system.

Correct option is (b)

33. For one elimensional box

$$\Psi = A\sin\frac{\pi x}{a}$$

$A = \sqrt{\frac{2}{a}}$ for one dimensional box normalisation constant

a = 200 nm

$$A = \sqrt{\frac{2}{200\ \text{nm}}} = \frac{1}{\sqrt{100\ \text{nm}}} = \frac{1}{10(\text{nm})^{½}} = 0.1(\text{nm})^{-½}$$

Correct option is (d)

GATE 2012

34. From Heisenberg uncertainty principle

$$\Delta x \Delta P_x \geq \frac{h}{4\pi}$$

In y coordinate, $\Delta y\ \Delta Py > \frac{\hbar}{2}$

Correct option is (d)

35. Selection rules for electronic transition for diatomic molecules are

$\Delta S = 0,\ \Delta\ell = 0, \pm 1$

$g \rightarrow u$ allowed

$+ \rightarrow +$ allowed

Correct option is (c)

36. Angular part $(\gamma_{\ell,m}(\theta\ \phi)) \propto \sin^2\theta\cos\theta\, e^{2i\phi}$

Compare with $e^{im\phi}$

m = 2

Function is 'f' orbital l = 3

$\ell = 3 \quad m = 2$

Correct option is (c)

37. Since the co-molecule is oriented along the z-axis, combination of ϕ_z^0 and ϕ_z^0 result in the formation of σ donating orbitals while combination of either ϕ_x^c and ϕ_x^c or ϕ_x^c and ϕ_x^c result in the formation of π bonding orbital.

The wave function of π bonding molecular orbital

$$c_1\phi_x^c + c_2\phi_x^0$$

Correct option is (d)

38. $$\int_{-\infty}^{\infty} N^2\psi\psi^* dT = 1$$

$$N^2\int_{-\infty}^{\infty}(2x^2-1)(2x^2-1)e^{-x^2/2}\ e^{-x^2/2}dx = 1$$

$$N^2\int_{-\infty}^{\infty}\left(\left(4\underset{(I_1)}{H^4}+\underset{(I_2)}{1}\right)-4\underset{I_3}{x^2}\right)e^{-x2/2} = \frac{1}{2}$$

$$I_1 = 4\int_{-\infty}^{+\infty}x^4\ e^{-x^2}dx \qquad \Rightarrow\ I_2 = 4\times 2\int_0^{\infty}x^4\ e^{-x^2}dx$$

$$I_1 = 4\times 2\times\frac{1}{2}\frac{\sqrt{5/2}}{(1)^{5/2}} = 4\times\frac{3}{2}\times\frac{1}{2}\sqrt{\pi} = 3\sqrt{\pi}$$

$$I_2 = \int_{-\infty}^{+\infty}x'\,e^{-x^2}dx = 2\int_{\infty}^{\infty}x'e^{-x^2}dx = 2.\frac{1}{2}\frac{\sqrt{½}}{(1)^{½}} = \sqrt{\pi}$$

$$I_3 = -4\int_{-\infty}^{+\infty}x^2e^{-x^2}\ dx = -4\times 2\int_0^{\infty}x^2e^{-x^2}\ dx = -4\times 2\times\frac{1}{2}\frac{\sqrt{3/2}}{(1)^{3/2}} = -2\sqrt{\pi}$$

$$N^2\left[3\sqrt{\pi}-2\sqrt{\pi}+\sqrt{\pi}\right] = 1 \quad\Rightarrow\quad N^2\left(2\sqrt{\pi}\right) = 1 \ \Rightarrow\ N = \left(\frac{1}{2\sqrt{\pi}}\right)^{½}$$

Correct option is (c)

39. $$\overset{1}{C}H_2 = \overset{2}{C}H-\overset{3}{C}H_2$$

Secular determine

$$\begin{vmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{vmatrix} \qquad \begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-Es_{33} \end{vmatrix}$$

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} \qquad \begin{array}{l} H_{11} = \alpha \\ H_{12} = \beta \\ S_{11} = 1 \\ S_{12} = 0 \end{array}$$

Correct option is (a)

40. Possible value of E

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} \text{ divided by } \beta$$

$$\begin{vmatrix} \frac{\alpha - E}{\beta} & 1 & 0 \\ 1 & \frac{\alpha - E}{\beta} & 1 \\ 0 & 1 & \frac{\alpha - E}{\beta} \end{vmatrix} \quad \text{let } \frac{\alpha - E}{\beta} = x \qquad ...(i)$$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} \text{solve the determinant.}$$

$x(x^2 - 1) - 1\ (x - 0) + 0$

$x(x^2 - 1) - 1\ (x - 0) + 0 \qquad x = 0$

$x^3 - x - x = x^3 - 2x = 0 x = \pm\sqrt{2}$

$x(x^2 - 2) = 0$

Put value of 'x' in equation (i)

$E = \alpha;\ E = \alpha - \sqrt{2}\beta;\ E = \alpha + \sqrt{2}\beta$

Correct option is (a)

GATE 2013

41. A trial wave function that can be expressed as a linear combination of 2 variational parameter leads to variational minimum energy $E_0 < E_2 < E_1$

Correct option is (c)

42. H_2 + dissociation energy = 2 h atom

–31.7eV + dissociation energy = 2 × (–13.6)

Dissociation energy = + 31.7 – 27.2 = 4.5

$$\begin{array}{ll} H+H \longrightarrow & H_2 \\ \downarrow & \downarrow \\ -13.6\text{ eV} & -31.7\text{eV} \end{array}$$

dissociation energy of H_2

$H_2 \longrightarrow H + H$

Correct option is (4.5)

43. Eigen function e^{-2x^2}

Operator $\left(\frac{d^2}{dx^2}-16x^2\right)$

For eigen value function operate by operator

$$\left(\frac{d^2}{dx^2}-16x^2\right)e^{-2x^2} \qquad \Rightarrow \frac{d^2}{dx^2}e^{-2x^2}-16x^2e^{-2x^2}$$

$$\frac{d}{dx}\frac{d}{dx}e^{-2x^2}-16x^2e^{-2x^2} \qquad \Rightarrow -4\frac{d}{dx}\times e^{-2x^2}-16x^2e^{-2x^2}$$

$$-4\left[x\,e^{-2x^2}(-4x)+e^{-2x^2}\right]-16x^2\,e^{-2x^2}-16x^2\,e^{-2x^2}$$

Eigenvalue = –4

Correct option is (b)

GATE 2014

44. The value of magnetic quantum number of p_x orbitial is undefined first of all fix the direction of applied magnetic field. Then decide the value of magnetic quantum number.

Correct option is (d)

45. $\psi_1\cdot\psi_2 = |\psi_1|^2|\psi_2|^2\cos\theta$

$$\cos\theta = \frac{\psi_1\cdot\psi_2}{|\psi_1|^2|\psi_2|^2}$$

$$\cos\ \theta = \frac{0.12\times0.12\psi_{35}\cdot\psi_{35}+0.63\times0.63\psi_{3px}\cdot\psi_{3px}+(0.77\times-0.77)\psi_{3Py}\cdot\psi_{3Py}}{\sqrt{(0.12)^2+(+0.63)^2+(0.77)^2}\sqrt{(0.12)^2+(-0.63)^2+(-0.77)^2}}$$

$$\cos\theta = \frac{(0.12\times0.12)+(0.63\times-0.63)+(0.77\times-0.77)}{\sqrt{(0.12)^2+(+0.63)^2+(0.77)2}\sqrt{0.0144+0.3969+0.5929}}$$

$$= 0.0144-0.3969-0.5929 = \frac{-0.9754}{\sqrt{1.0042}\sqrt{1.0042}}$$

$$\cos\theta = \frac{-0.9754}{1.1} \qquad \cos\theta = -0.9754$$

$$\theta = \cos^{-1}(-0.9754) = 179$$

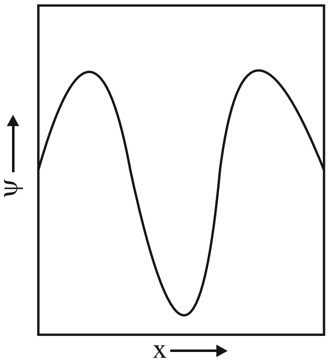
GATE 2015

46. $$-\frac{\hbar^2}{c}\frac{\partial^2}{\partial x^2}e^{-ikx} \Rightarrow -\hbar^2\frac{\partial}{\partial x}\frac{\partial}{\partial x}e^{-ikx} \Rightarrow -\hbar^2\frac{\partial}{\partial x}[-ik]e^{-ikx}$$

$$\Rightarrow -\hbar^2(-ik)\frac{\partial}{\partial x}e^{-ikx} \Rightarrow \hbar^2(-ik)(-ik)e^{-ikx} \Rightarrow k^2\hbar^2$$

Correct option is (a)

47.



It is an acceptable wavefunction because function is single valued and continuous.

Correct option is (d)

48. $$E_n = \frac{n^2\hbar^2}{8m\ell^2}; E_1 = \frac{(1)^2\hbar^2}{8m(0.2)^2 mn^2} \Rightarrow E_1 = \frac{\hbar^2}{8\times 9.1\times 10^{-31}\,kg\times 0.2\times 0.2\times 10^{-9}\,mtr\times 10^{9}\,mtr}$$

$$E_2 = \frac{(1)\hbar^2}{8\times 9.1\times 10^{-31}\,kg\times 2\times 2\times 10^{-9}\,mtr\times 10^{-9}\,mtr}$$

$$E_1 - E_2 = \frac{\hbar^2}{8\times 9.1\times 10^{-31}\,kg\times 10^{-18}\,mtr^2}\left[\frac{1}{0.04}-\frac{1}{4}\right]$$

$$E_1 - E_2 = \frac{6.63\times 6.63\times 10^{-34}\,J.S\times 10^{-34}\,J.S}{8\times 9.1\times 10^{-31}\,kg\times 10^{-18}\,mtr^2}\left[\frac{100}{4}-\frac{1}{4}\right]$$

$$E_1 - E_2 = \frac{6.63\times 6.63\times 10^{-34}\,J.S\times 10^{-34}\,J.S}{8\times 9.1\times 10^{-31}\,kg\times 10^{-18}\,mtr^2}\times\frac{99}{4}$$

$E_1 - E_2 = 896$

Correct option is (896 to 900)

GATE 2016

49. Linear momentum = $p_x \Rightarrow -i\hbar \frac{\partial}{\partial x}$

$\Rightarrow -i\hbar \frac{\partial}{\partial x} e^{-ikx} \frac{\partial}{\partial x}(-ikx) \quad \Rightarrow i\hbar\,(-ik)\, e^{-ikx} \frac{\partial}{\partial x}$

$\Rightarrow -i\hbar(-ik)\, e^{-ikx}(1)$

$\Rightarrow i \times i\, \hbar k\, e^{-ikx} \Rightarrow -\hbar k\, e^{-ikx}$

eigenvalue ($-\hbar k$)

Correct option is (d)

50. Energy for He atom $\frac{En > -13.6(2)^2}{(1)^2} = -13.6(4)$

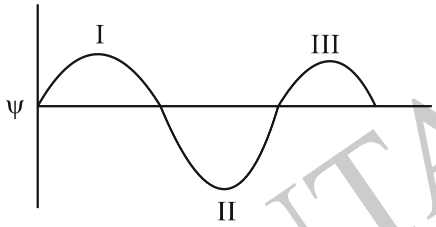
I.p. hydrogen = 13.6 V

I.p. Hecting = 24.6 eV

growing state for He = $-14(13.6) - 24.6$

Correct option is (b)

51.



Probability = $\int_{L,L}^{UL} \psi^2 d\tau$

More ψ region more probability, (P) II > III > I

Correct option is (b)

GATE 2017

52. For ortho hydrogen,

Nuclear wave function → symmetric

Rotational quantum number → symmetric → odd

Correct option is (b)

53. $K = \frac{n\pi}{L}$; $\qquad K = \frac{2\pi}{\lambda}$

$\frac{2\pi}{\lambda} = \frac{n\pi}{L}$; $\qquad \lambda = \frac{2L}{n}$

Correct option is (a)

54. Lowest energy in simple harmonic oscillator is $\frac{1}{2}h\nu$

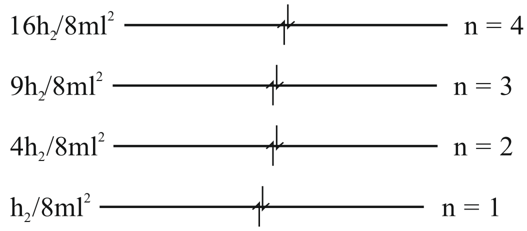
$$E_n = \left(n + \frac{1}{2}\right)\hbar\nu$$

$$\frac{7}{2}\hbar\nu \rightarrow n = 3;\ \frac{5}{2}\hbar\nu \rightarrow n = 2;\ \frac{3}{2}\hbar\nu \rightarrow n = 1; \frac{1}{2}\hbar\nu \rightarrow n = 0; \frac{1}{2}\hbar\nu = 300\text{cm}^{-1}$$

$$E_1 = \frac{3}{2}\hbar\nu = 3 \times \frac{1}{2}\hbar\nu = 3 \times 300\ \text{cm}^{-1} = 900\ \text{cm}^{-1}$$

Correct answer is (900)

55.



$$\Delta\varepsilon = \frac{(4h)^2}{8m\ell^2} - \frac{(3h)^2}{8m\ell^2}, \quad \ell = 0.70\ \text{nm}$$

$$h\nu = \frac{3 \times h^2}{8m\ell^2} \qquad \frac{hc}{\lambda} = \frac{7h^2}{8m\ell^2} \Rightarrow \lambda = \frac{hc \times 8m\ell^2}{7h^2} \Rightarrow \lambda = \frac{8 \times m \times \ell^2 \times c}{7 \times h}$$

$$= \frac{8 \times 9.1 \times 10^{-31} \times 3 \times 10^8\,\text{m/s} \times 0.70 \times 10^{-9} \times 0.70 \times 10^{-9}}{7 \times 6.63 \times 10^{-34}\,\text{J/s}} = 2.3.07 \times 10^{-7}\ \text{m} = 230.7\ \text{nm}$$

Correct answer is (225 to 240)

56. $$\cos\theta = \frac{m\ell}{\sqrt{\ell / \ell + 1}} = \frac{2 \times 2}{\sqrt{2(2+1)}} = \frac{4}{\sqrt{6}}$$

$$\theta = \cos^{-1}\frac{4}{\sqrt{6}} = 33.60 \text{ to } 36.90$$

Correct answer is (33.60 to 36.90)

57. $$\psi = \left[C\phi_1 - \left(\frac{1}{\sqrt{3}}\right)\phi_2\right]$$

for normalized

$$C^2 + C_2^2 = 1;\ C^2 + \left(\frac{1}{\sqrt{3}}\right)^2 = 1;\ C^2 + \frac{1}{3} = 1;\ C^2\ 1 - \frac{1}{3};\ C^2 = \frac{2}{3}$$

$$C = \sqrt{\frac{2}{3}} = \frac{\sqrt{2}}{\sqrt{3}} = \frac{1.414}{1.732} = 0.81$$

Correct answer is (0.81)

GATE 2018

58. $L^2 = L_x^2 + L_y^2 + L_z^2$ ...(i)

$L = \sqrt{\ell(\ell+1)-\hbar};\ L_z = m\hbar$

From eqation (1),

$L^2 - L_z^2 = L_x^2 + L_y^2\,;\ \left(\sqrt{\ell(\ell+1)}.\hbar\right)^2 - (m\hbar)^2 = L_x^2 + L_y^2$

$\Rightarrow \ell\,(\ell + 1).\hbar^2 - m^2\hbar^2 \quad \Rightarrow \quad \left(\ell(\ell+1)-m^2\right)\hbar^2$

Correct option is (a)

59. $[a_+, a_-] = \dfrac{1}{\sqrt{2}}\dfrac{1}{\sqrt{2}}[x+ip_x, x-ip_x]\psi$

$$= \frac{1}{2}\left[(x+ip_x)(x-ip_x)\psi-(x-ip_x)(x+ip_x)\psi\right]$$

$$= \left[(x+ip_x)(x\psi-ip_x\psi)-(x-ip_x)(x\psi+ip_x\psi)\right]$$

$$= x^2\psi - ixp_x\psi + ip_x(x\psi) - iip_x^2\psi - x^2\psi - ixp_x\psi + ip_x(x\psi) + iip_x^2\psi$$

$$= x^2\psi - ixp_x\psi + i(-i\hbar)\frac{d}{dx}(x\psi) - iip_x^2\psi - x^2\psi - ixp_x\psi + i(x\hbar)\frac{d}{dx}(x\psi) - iip_x^2\psi$$

$$= x^2\psi - ixp_x\psi + i(-i\hbar)\left[x\frac{\partial\psi}{dx}+\psi\right] - iip_x^2\psi - x^2\psi - ip_x\psi + i(i\hbar)\left[x\frac{d\psi}{dx}+\psi\right] - iip_x^2\psi$$

$$= x^2\psi - ixp_x\psi + ixp_x\psi + \hbar - iip_x^2\psi - x^2\psi - ixp_x\psi + \hbar + iip_x^2\psi = \frac{1}{2}2\hbar = \hbar$$

Correct option is (c)

60. $H_2 \rightarrow 2H$

$\therefore\ E_{\text{disconnected}} \quad = \text{Energy of H-atom} \times 2 = \text{Energy of } H_2$

$\quad = \ 2 \times (-13.6) - (-31.70) = 4.5\ \text{eV}$

Correct Answer is 4.5

61. For molecule XY if ψ_x and ψ_y are normalized atomic orbital for atoms X and Y

$$\psi_+ = \underset{\displaystyle C_1}{\underset{\downarrow}{0.56\psi_x}} + \underset{\displaystyle C_2}{\underset{\downarrow}{0.56\psi_y}}$$

$C_1^2 + C_2^2 + 2C_1C_2S_{XY} = 1$ where, S_{XY} = overalp integral

$(0.56)^2 + (0.56)^2 + 2 \times 0.56 \times 0.56 \times S_{XY} = 1 \quad \{S_{XY} = 0.59\}$

62. $$\text{Probability} = \frac{N_J}{N} = \frac{w^{-E_J/k_BT}}{q_{\text{vibration}}}$$

$$E_{\text{ground state}}\ \frac{1}{2}\ h\nu$$

$$P = \frac{e^{-1/2h\nu n/kBT}}{\frac{e^{-h\nu/2k_BT}}{e^{-h\nu/k_BT}}} = 1 - e^{-h\nu/k_BT} = 1 - e^{-3} \Rightarrow P = 0.95$$

63. $$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/2} e^{-ax^2},\ H_P(x) = \frac{1}{6}\gamma x^3,\ \omega = \sqrt{\frac{k}{\mu}} = \left(\frac{k}{\mu}\right)^{1/2}$$

First order correction in ground state

$$E_0^{(1)} = \int_{-\infty}^{+\infty} \psi_0^* \, H_P \psi_0(x)dx = \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{+\infty} e^{-2ax^2}\left(\frac{1}{6}\gamma x^3\right)dx$$

$$= \frac{\gamma}{6}\left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty+\infty} e^{-2ax^2} x^3 dx = 0$$

Total energy corrected to first order

$$E_0 = E_0^0 + E_0^{(1)} = \frac{1}{2}\hbar\omega + 0 = \frac{1}{2}\hbar\left(\frac{k}{\mu}\right)^{1/2}$$

Correct option is (a)

64. The longest wavelength absorption in the benzene spectrum according to model

$$\frac{hc}{\lambda} = E_2 - E_1 = \frac{\hbar^2}{2mR^2}\left[2^2 - 1^2\right]$$

$$\frac{hc}{\lambda} = \frac{\hbar^2}{2mR^2}\left[2^2 - 1^2\right]$$

$$\frac{hc}{\lambda} = \frac{\hbar \times \hbar}{4\pi^2 \times 2mR^2} \Rightarrow \frac{c}{\lambda} = \frac{h}{8\pi^2 mR^2}$$

$$\frac{c}{\lambda} = \frac{h}{8\pi^2 mR^2}$$

$$= \frac{3\times 10^8\,\text{m/sec}}{\lambda} = \frac{6.6\times 10^{-34}\,\text{J-sec}\times 3}{8\times 3.14\times 3.14\times 9.1\times 10^{-31}\text{kg}\times 1.4\times 10^{-10}\,\text{mtr}\times 1.4\times 10^{-10}\,\text{mtr}}$$

$$\lambda = \frac{8\times 3.14\times 3.14\times 9.1\times 10^{-31}\text{kg}\times 1.4\times 10^{-10}\times 1.4\times 10^{-10}\,\text{mtr}^2\times 3\times 10^8\,\text{m/sec}}{6.63\times 10^{-34}\,\text{J-sec}\times 3}$$

$$\lambda = 212.9 \times 10^{-9}\ \text{mtr}$$

$$\lambda = 212.1\ \text{nm}$$

GATE 2019

65.Sol. $\psi(x) = \sin kxe^{3ikx}$

$$\langle \psi | \psi \rangle = \int_{-\infty}^{\infty} \psi^* \psi dx$$

$$= \int_{-\infty}^{\infty} \sin^2 kxdx$$

$$\langle P \rangle = ?$$

$$P|\psi\rangle = -i\hbar \frac{1}{\sqrt{x}}\left[\sin kxe^{3ikx}\right]$$

$$= -i\hbar\left[(3ik)\sin kxe^{3ikx} + k\cos kxe^{3ikh}\right]$$

$$= -i\hbar[(3ik)\sin kx \to (k)\cos kx]e^{3ikx}$$

$$\langle P \rangle = \frac{\langle \psi | P | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$= \frac{\int \sin kxe^{-3ikx}(-i\hbar[(3ik)\sin kx + (k)\cos kx])e^{3ikx}dx}{\langle \psi | \psi \rangle}$$

$$= \frac{-i\hbar\left[\int\limits_{-\infty}^{\infty}(3ik)\sin^2 kxdx + (k)\int\limits_{-\infty}^{\infty}\sin kx\cos kxdx\right]}{\int\limits_{-\infty}^{\infty}\sin^2 kxdx}$$

$$= -i\hbar\left[\frac{(3ik)\int\limits_{-\infty}^{\infty}\sin^2 kxdx}{\int\limits_{-\infty}^{\infty}\sin^2 kxdx} + \frac{k}{2}\frac{\int\limits_{-\infty}^{\infty}\sin^2 kxdx}{\int\limits_{-\infty}^{\infty}\sin^2 kxdx}\right]$$

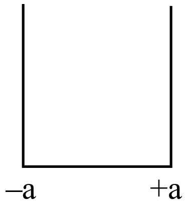
$$= (i\hbar)(3ik) = 3\hbar k$$

$$\langle P \rangle = 3\hbar k$$

66.Sol. Length of box is 2a, between limits –a to a

$\Delta H = V' = Cx$

Wavefunction for 1st excited state for such a system is



$$\psi_2 = \sqrt{\frac{1}{a}}\sin\frac{2\pi x}{2a}$$

$$\psi_2 = \sqrt{\frac{1}{a}}\sin\frac{\pi x}{a}$$

1st order correction would be

$$\Delta E_2^{(1)} = \int \psi_2^* \Delta H \psi_2 dx$$

$$= \int \sqrt{\frac{1}{a}}\sin\frac{\pi x}{a} Cx \sqrt{\frac{1}{a}}\sin\frac{\pi x}{a} dx$$

$$\Delta E_2^{(1)} = 0$$

67.Sol. $\left\langle \alpha \,|\, \hat{S}_x\hat{S}_y - \hat{S}_y\hat{S}_x \,|\, \alpha \right\rangle = i\hbar^2 a$

$$\left\langle \alpha \,|\, S_n, S_y \,|\, \alpha \right\rangle = i\hbar^2 a$$

$$\left[\begin{array}{c} |\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ \langle\alpha| = \begin{pmatrix} 1 & 0 \end{pmatrix} \\ \text{also } S_z = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \end{array}\right]$$

$$\left\langle \alpha \,|\, i\hbar S_z \,|\, \alpha \right\rangle = i\hbar^2 a$$

$$\Rightarrow \qquad i\hbar\left\langle \alpha \,|\, S_z \,|\, \alpha \right\rangle = i\hbar^2 a$$

$$i\hbar\left\langle \alpha \,|\left(\frac{\hbar}{2}\right)\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}|\, \alpha \right\rangle = i\hbar^2 a$$

$$\frac{i\hbar^2}{2}\left[[1 \quad 0]\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix}\right] = i\hbar^2 a$$

$$\frac{1}{2}(1) = a$$

$$a = \frac{1}{2}$$

$$a = 0.5$$

68.Sol. $W_x = 6.5 \times 10^{14}$ rad $s^{-1} = 10.35 \times 10^{13}$ sec^{-1}

$W_y = 3.25 \times 10^{14}$ rad $s^{-1} = 5.175 \times 10^{13}$ sec^{-1}

Energy of ground state in sec^{-1}

$$E_{(0,0)} = \left(0 + \frac{1}{2}\right)v_x + \left(0 + \frac{1}{2}\right)v_y$$

$$= 25.875 \times 10^{13}\ \text{sec}^{-1}$$

Wavelength required for transition is equal to energy difference between two states,

$$\Delta E = 25.875 \times 10^{13} - 15.525 \times 10^{13}$$

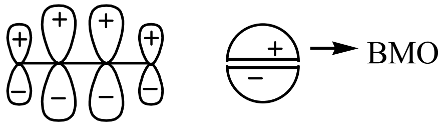
$$\Delta E = 10.35 \times 10^{13}\ \text{sec}^{-1}$$

in 'm' $\lambda = 2.89 \times 10^{-6}\,\text{m}$

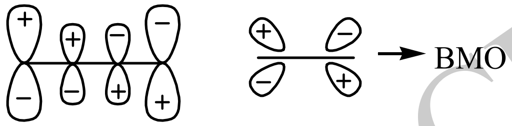
$$\lambda = 2.9 \times 10^{-6}\,\text{m}$$

GATE 2020

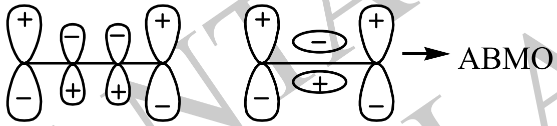
69.Sol.: $\Psi_1 = 0.372\ \phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.37\phi_4$



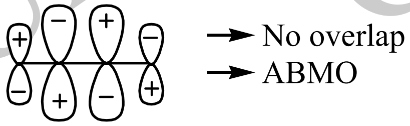
$$\Psi_2 = 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4$$



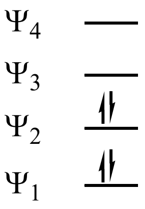
$$\Psi_3 = 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4$$



$$\Psi_4 = 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4$$



Butadiene have 4π electron



Lowest unoccupied π-molecular orbital is Ψ_3

Correct option is (a)

70Sol.: Radial mode, $R_{3,0} = 0$

$$R_{3,0} = \frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-2\rho+\frac{\rho^2}{a}\right)e^{-\rho/6}$$

$$\rho = \frac{2zr}{a_0}$$

For hydrogen atom, $(Z = 1)$

$$R_{3,0} = \frac{1}{9\sqrt{3}}\left(\frac{1}{a_0}\right)^{3/2}\left(6-\frac{4r}{a_0}+\frac{4r^2}{9a_0^2}\right)e^{-\frac{r}{3a_0}} = 0$$

$$\left(6-\frac{4r}{a_0}+\frac{4r^2}{9a_0^2}\right) = 0$$

$$\Rightarrow \qquad 27-\frac{18r}{a_0}+\frac{2r^2}{a_0^2} = 0$$

$$2r^2 - 18a_0r + 27a_0^2 = 0$$

$$r = \frac{+18a_0 \pm \sqrt{(-18a_0)^2 - 4\times 2\times 27a_0^2}}{2\times 2}$$

$$r = \frac{+18a_0 \pm \sqrt{108a_0^2}}{4}$$

$$r = \frac{+18a_0 \pm 6\sqrt{3}\,a_0}{4}$$

$$r = \left(\frac{9\pm 3\sqrt{3}}{2}\right)a_0$$

Correct option is (c)

71.Sol.: Given; Trial wave function

$$f = x(a-x) \quad 0 \le x \le a$$

To find; ^ error in ground state energy of particle in 10 box

Also given; true ground state energy of above system is $\frac{\hbar^2}{8ma^2}$; $\int_0^a \psi^*\psi d\tau = \frac{a^5}{30}$

Solution for given trial wave function

$$E = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \quad \text{... (1)}$$

$$E = \frac{\frac{-\hbar^2}{2m}\int_0^a x(a-x)\frac{d^2}{dx^2}\left[x(a-x)\right]}{a^5/30} \quad \text{... (2)}$$

Solving for $\frac{d^2}{dx^2}\left[x(a-x)\right]$

$$\frac{d^2}{dx^2}\left[x(a-x)\right] = \frac{d}{dx}\left[xa - x^2\right] = \frac{d}{dx}\left[(a-2x)\right]$$

$$\frac{d^2}{dx^2}\left[x(a-x)\right] = -2 \quad \text{... (3)}$$

Put (3) in (2)

$$E = \frac{-\hbar^2}{2m}\int_0^a x(a-x)(-2)$$

$$E = \frac{\hbar^2}{m}\int_0^a x(a-x)$$

Solving for above integral weget

$$E = \frac{5\hbar^2}{4\pi ma^2} = \frac{0.126\hbar^2}{ma^2} \quad \text{... (4)}$$

given $E_0 = \frac{1}{8}\frac{\hbar^2}{ma^2}$

$$E_0 = 0.125\frac{\hbar^2}{ma^2} \quad \text{... (5)}$$

Percentage error is calculates by

$$= \frac{0.1266 - 0.125}{0.125} \times 100$$

Percentage error = 1.32

GATE 2021

72.Sol. The ****** wavelength of an argon atom is given by

$$\lambda = \frac{h}{m\nu} \text{ (m = mass of argon atom)}$$

$$\lambda = \frac{6.626\times10^{-34}\,\text{kg m}^2\text{s}^{-1}}{\frac{40}{\text{NA}}\times30^{-3}\,\text{kg}\times250\,\text{m s}^{-1}}$$

$$\lambda = \frac{6.626\times10^{-3}\times6.022\times10^{23}\times\text{kg m}^2\text{s}^{-1}}{40\times10^{-3}\,\text{kg}\times250\,\text{ms}^{-1}}$$

$\lambda = 4 \times 10^{-11}$ m

$= 40 \times 10^{-11}$ m

$= 40$ pm

73 Sol. Condition for acceptable wave function:

1. It should be single valued
2. It can be odd or even but not necessarily are of them.
3. It should be continoues

Correct option are (b) and (d)

2

THERMODYNAMICS & THERMOCHEMISTRY

GATE 2005

1. In adiabatic system, $q = 0$ $\Delta U = w$

   Hence, work is independent of path from A to B.

   Correct option s (b)

2. $\Pi_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$

   For real gas, $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ and $\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{V - b}$

   So, $\Pi_T = \frac{T \cdot R}{V - b} - P$

   $\Pi_T = \frac{RT}{V - b} - \left\{\frac{RT}{V - b} - \frac{a}{V^2}\right\}$

   $\Pi_T = \frac{a}{V^2}$

   Correct option is (a)

3. $S = R \text{ In } W$

   $S = 8.314 \text{ In } 2$

   $S = 5.76 \text{ J mol}^{-1}$

   Correct option is (d)

4. When hydrogen adsorption on a platinum surface the entropy decreases and Gibbs free energy is negative.

   During adsorption heat released and free energy is decreases so randomness is decreases

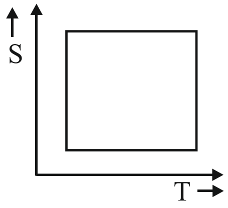
   $\Delta H = \Delta H - T\,\Delta S$

   $\{\Delta G = -ve, \Delta S = -ve\}$

   Correct option is (c)

GATE 2006

5. Plot describing carnot cycle is



Correct option is (a)

6. $N_2 + 3H_2 \rightarrow 2\ NH3$

$\Delta S^0_{univ} = -197 + 308 = 111\ J\ K{-}1$

$= -197 + \frac{91800}{298}$

$\Delta S^0_{univ} = -197 + 308 = 111\ J\ K^{-1}$

$\Delta S^0_{sys} = -197\ J\ K^{-1}$

$\Delta H^0_{sys} = -91.8\ kJ$

$= -91800\ J$

$\Delta H^0_{surr} = \Delta H^0_{sys}$

$= 97800\ J$

Correct option is (d)

7. $w = -P\ \Delta\ V$

$= -\ 20\ (10 - 0.5) = -\ 20 \times 9.5$

$w = -\ 190$ atm L

or $|w| = 190$ atm L

Correct option is (c)

8. Above process is isothermal

Therefore, $\Delta H = \Delta E$

Correct option is (d)

GATE 2007

9. Chemical potential is $\left(\frac{\partial E}{\partial n_i}\right)_{s_1 v_1 n_j}$

Correct option is (a)

10. $\Delta T = 75 - 15 = 60°$

$w = 54$ g of H_2O = 3 moles of H_2O

At constant pressure, $\Delta H = q_p$

$q_p = n\ C_{v,m}\ \Delta T$ or $\Delta H = 3 \times 75 \times 60 = 13500\ J = \boxed{13.5\ kJ}$

Correct option is (b)

11. $V_\ell = 1.001\ mLg^{-1}\ ;\ V_s = 1.0907\ mLg^{-1}$

$H_2O(s) \rightleftharpoons H_2O(\ell)$

$$\frac{dP}{dT}=\frac{\Delta H_{fusion}}{T\Delta V}=\frac{333.88}{273\times(1.001-1.0907)}$$

$$\frac{dP}{dT}=\frac{333.88}{273\times(1.001-1.0907)}=\frac{Jg^{-1}}{K(mLg^{-1})};\frac{dP}{dT}=-13.634\ J\ K^{-1}\ mL^{-1};\ w=PV$$

Unit of $P=\frac{w}{V}=J\ mL^{-1}$

Now, $1\ Pa = 1\ J\ m^{-3}$; $1\ Pa=\frac{1\ J}{m^3}$; $1\ Pa=\frac{1\ J}{10^6\ mL}$; $10^6\ Pa = 1\ J\ mL^{-1}$

$$\Rightarrow\ \frac{dP}{dT}=-\ 13.634\times10^{6}\ Pa\ K^{-1}$$

Now, $1\ atm = 1.01325\times10^5\ Pa$ or

$$1\ Pa=\frac{1\times10^{-5}}{1.01325}=-0.9869\times10^{-5}$$

$$\Rightarrow\ \frac{dP}{dT}=-\ 13.634\times10^{6}\times0.9869\times10^{-5}\ atm\ K^{-1}$$

$$\frac{dP}{dT}=-\ 13.455\times10\ atm\ K^{-1},\text{ or}$$

$$\frac{dP}{dT}=-\ 134.55\ atm\ K^{-1}$$

Hence $\frac{dP}{dT}=\frac{1}{134.55}=-0.0074\ atm^{-1}\ K$ or $-0.0074\ atm^{-1}\ {}^\circ C$.

Correct option is (a)

12. $\Delta S_{mix}=-nR\sum x_i\ In\ x_i=-20\times8.314\left\{\frac{1}{2}In\frac{1}{2}+\frac{1}{2}In\frac{1}{2}\right\}$

$\Delta S_{mix}=115.3\ J\ K^{-1}$

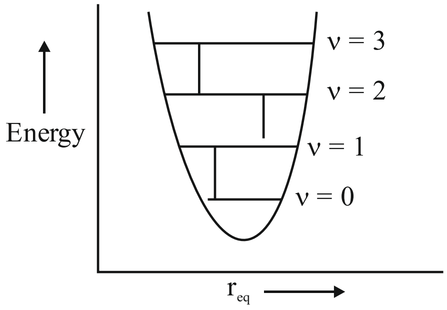
Correct option is (a)

13. (I) Correct statements are

(1) $\Delta E_{0\to1}=hv$

(2) $\Delta E_{0\to2}=hv$

(3) $\Delta E_{2\to3}=hv$



Gap equally spaced

(II) In fluorescence transition from a singlet electronic state to another singlet electronic state by absorption of light

Correct option is (c)

GATE 2008

14. Residual entropy for $N_2O = 5.8\ JK^{-1}\ mol^{-1}$

Number of orientations = ?

S = R In W; W = ?

$$5.8\ JK^{-1}\ mol^{-1} = \frac{8.314\ J}{K^{-1} mol} \times 2.303 \log_{10} W; \log W = 0.3025 \simeq 0.3010; \log W = \log 2$$

$\boxed{W = 2}$

Correct option is (c)

15. P(V – nb) = nRT

$$C_P - C_V = T\ T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_v$$

Now, for an equation P(V–nb) = nRT

or PV – P nb = nRT

Differentiate w.r.t. T at constant P

$$P\left(\frac{\partial V}{\partial T}\right)_P + 0 = nR$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

Again for equation, PV – Pnb = nRT

Differentiate w.r.t T at constant V

$$V\left(\frac{\partial P}{\partial T}\right)_V - nb\left(\frac{\partial P}{\partial T}\right)_v = nR$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb} \Rightarrow C_p - C_v \text{ for equation is } T\cdot\frac{nR}{P}\times\frac{nR}{V-nb} = \frac{(nRT)nR}{P(V-nb)}$$

$C_p - C_v = nR$; $(C_p - C_v)_{ideal} = nR$

So, $\frac{C_p - C_v}{(C_p - C_v)_{ideal}} = 1$

Correct option is (c)

GATE 2009

16. $q = \omega.C_S\Delta T$

(a) $q = 200\ C_S\ (80 - 40)$

$q = 8000\ C_S$

(b) $q = 100\ C_S\ (80 - 20)$

$q = 6000\ C_S$

(c) $q = 150\ C_S\ (80 - 50)$

$q = 4500\ C_S$

(d) $q = 300\ C_S\ (80 - 30)$

$= 15000\ C_S$

Correct option is (c)

17. If $\Delta ng < 0 \Rightarrow$ decrease in entropy.

In option (a) $\Delta ng < 0$

Correct option is (a)

18. $2NO(g) + O_2\ (g) \longrightarrow 2NO_2\ (g)$

$\Delta H = 2 \times \Delta H_f^0\ (NO_2) - \{2 \times \Delta H_f^0\ (NO) + \Delta H_f^0\ (O_2)\}$

$\Delta H = 2 \times 33.2 - \{2 \times 90.3 + 0\}$; $\Delta H = -114.2$ kJ.

Correct option is (c)

19. $\Delta G = nRT\ In; \left(\frac{P_2}{P_1}\right)$; $\Delta G = 1\ RT\ In\ \left(\frac{2}{1}\right)$; $\Delta G = RT\ In\ 2$

Correct option is (a)

GATE 2010

20. $S = k\ In\ w$

$S = k\ In\ (arrangement)^{NA}$

$S = k.\ NA\ In\ (2)$

$\boxed{S = R\ In\ 2}$ arrangement $\boxed{C \equiv O}$, $\boxed{O \equiv C}$

Correct option is (a)

21. Ideal gas, $\boxed{PV = RT}$

$$\left(\frac{dP}{dT}\right)_v = \frac{d}{dT}\left(\frac{RT}{V}\right)_v \frac{R}{V}\frac{dT}{dT} = \frac{R}{V}$$

$$\left(\frac{dT}{dV}\right)_v = \left(\frac{d}{dV}\left(\frac{PV}{R}\right)\right)_P \frac{P}{R}\frac{dV}{dV} = \frac{P}{R}$$

$$\left(\frac{dV}{dP}\right)_T = \left(\frac{d}{dP}\left(\frac{RT}{P}\right)\right)_T = RT\frac{dP^{-1}}{dP} = -\frac{RT}{P^2}$$

$$\left(\frac{dP}{dT}\right)_V = \left(\frac{dT}{dV}\right)_P\left(\frac{dV}{dP}\right)_T = \frac{R}{V}\times\frac{P}{R}\times\frac{-RT}{P^2} = \frac{P\times P\times(-RT)}{RT\times P^2} = -1 \qquad \because V = \frac{RT}{P}$$

Correct option is (b)

22. Internal energy u and entropy S are state function as they depend only on the initial and final state of the system. They follow Euler thorem and for this cyclic integral is zero.

23. $\Delta S = nC_V \text{ In } \frac{T_2}{T_1} \qquad \Rightarrow \Delta S = 2 \times \frac{3}{2} R \text{ In } \frac{T_2}{T_1}$

$\Delta S = 2\times\frac{3}{2} \times 8.314 \times 2.303 \times \log \frac{500}{300} \qquad \Rightarrow \Delta S = 3 \times 8.314 \times 2.303 \log 5 - \log 3$

$\Delta S = 3 \times 8.314 \times 2.303\,[0.6990 - 0.4771] = 3 \times 8.314 \times 2.303 \times 0.2219$

$= 12.74 \text{ J/K} = \frac{12.74 \text{ J}}{2k - \text{mole}} = 6.37 \text{ J/K} - \text{mole}$

Correct option is (c)

24. $\text{In } \gamma = \int_0^P \frac{z-1}{P} dP \qquad \Rightarrow \text{In } \gamma = \int_0^P \frac{1+\frac{Pb}{RT}-1}{P} dP \qquad P(V-b) = RT$

$\text{In } \gamma = \int_0^P \frac{Pb}{RT} dP \qquad \Rightarrow \frac{bP}{RT} \qquad PV - Pb = RT$

$\boxed{\gamma = e^{bP/RT}} \qquad \frac{PV}{RT} = \frac{RT}{RT} + \frac{Pb}{RT}$

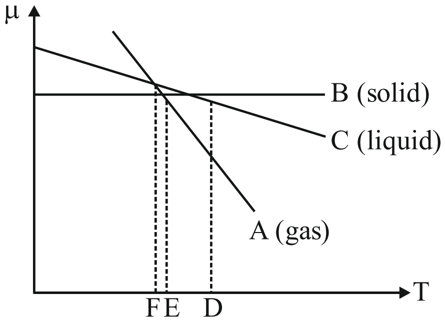
$\boxed{Z = 1 + \frac{Pb}{RT}}$

Correct option is (d)

But W and U are path and depend only the path followed not follow Euler theorem cyclic integral is not zero.

Correct option is (d)

25.



Correct option is (d)

GATE 2011

26. $dG = VdP - SdT$ (from Maxwell)

At constant temperature $dT = 0$

$$\left(\frac{dG}{dp}\right)_T = V$$

Correct option is (a)

27. $$\Delta S = nCp\ In\frac{T_2}{T_1} + nR\ In\frac{P_1}{P_2}$$

$$\Delta S = nCp\ In\frac{T_2}{T_1} + R\ In\frac{P_1}{P_2}$$

$$= 2.303 \times \frac{3}{2} \times 8.314 \log\frac{200}{300} + 2.303 \times 8.314 \log\frac{1}{10}$$

(for manoatomic)

$$= 2.303 \times \frac{5}{2} \times 8.314 \times \log\frac{2}{3} + 2.303 \times 8.314 \times (\log 1 - \log 10)$$

$$= 47.86 \times \log\frac{2}{3} - 19.14 = -8.42 - 1914 = -27.56 J/K - mol$$

Correct option is (a)

GATE 2013

28. $\Delta U = \Delta H - T\Delta S$

$\Delta H = \Delta U + \Delta ngRT$ $\qquad$ $X_2O_4(\ell) \longrightarrow 2 \times O_2\ (g)$

$= 9kJ + 4.955\ kJ = 13.955\ kJ$ $\qquad$ $\Delta ng = 2 - 0 = 2$

$\Delta G = 13.955\ kJ - 298 \times 0.84 = 13.955\ kJ - 25.032\ kJ = -11.08\ kJ$

Correct option is (a)

29. $\Delta S = \dfrac{\Delta H}{T_b} \Rightarrow T_b = 353\ \text{K}$

$\Delta H = \Delta S_{vap} \times T_b; \quad \Delta S_{vap} = 87\,\text{J/K} - \text{mol}$

$\Delta H = 87 \times 353\ \text{J/mol}$

For 3 mole = 92.1 3 kJ

Correct option is (92.13)

GATE 2014

30. Maximum non-PV work is equal to ΔG.

Correct option is (b)

31. $A + B \rightleftharpoons C$

Thermodynamic equation constant is dimensionless.

If equilibrium constant is k_p

$$k_p = \frac{\left(\dfrac{P_C}{P^{\phi}}\right)}{\left(\dfrac{P_B}{P_A^{\phi}}\right)\left(\dfrac{P_A}{P^{\phi}}\right)} = \text{unit less} \quad \text{where, } P^{\phi} = \text{standard state pressure}$$

Correct option is (d)

32. E = 0.55

$T_C = 105°\text{C} = 378\ \text{K}$

$T_H = ??$

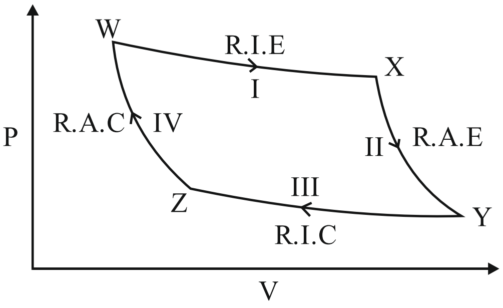
$$E = \frac{T_H - T_C}{T_H} \Rightarrow 0.55 = 1 - \frac{T_C}{T_H} \Rightarrow \frac{T_C}{T_H} = 0.45$$

$$T_H = \frac{378}{0.45} = 840\ \text{K}$$

Correct option is (840)

GATE 2015

33.



In isothermal process, $\Delta U = 0$

In adiabatic process, $\Delta U \neq 0$

Correct option is (b)

34. $dU = TdS - PdV; \left(\frac{\partial V}{\partial S}\right)_v = T$

Correct option is (a)

35. For and ideal gas, $U = 3.5\ PV + K$

or $U = 3.5\ RT + K$

$dU = 3.5\ R\ dT$

$\Delta U = 3.5\ R\ (T_2 - T_1)$

$V_1 = 0.25\ m^3$ $\quad P_1 = 5\ Nm^{-2}$ $\quad PV^{1.3} = \text{constant}$

$V_2 = 0.86\ m^3$ $\quad \Delta U = ??$ $\quad \gamma = 1.3$

At initial state, $P_1V_1 = RT_1$

$$T_1 = \frac{5 \times 0.25}{8.314} = 0.1503\ K$$

Since expansion is adiabatic, $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}; T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 0.1503 \times \left(\frac{0.25}{0.86}\right)^{0.3}$

$T_2 = 0.1035\ K$

$\Delta U = 3.5\ R(T_2 - T_1) = 3.5 \times 8.314\ (0.1035 - 0.1503)$

$\Delta U = -1.36\ J$

Correct option is (–1.38 to –1.39)

36. $\Delta S = \int \frac{nC_{p,m}}{T}\ dT$ at constant pressure

$$\Delta S = \int \frac{5 + 0.1T}{T} dT; \Delta S = \int_{300}^{400} \frac{5}{T}\ dT + \int_{300}^{400} 0.1\ dT$$

$$\Delta S = 5\mathrm{In}\left(\frac{400}{300}\right) + 0.1\ (400\text{–}300); \Delta S = 1.438 + 10$$

$\Delta S = 11.438\ JK^{-1}\ mol^{-1}$

Correct option is (11.3 to 11.5)

GATE 2016

37. $\Delta S = n \ln\left(\frac{V_2}{V_1}\right)$ at constant temperature

$\Delta S = 8.314 \ln\left(\frac{2}{5}\right)$; $\Delta S = -7.61\ JK^{-1}$

Correct answer is (–7.61)

38. Correct criterion, is $(\Delta G)_{T,P} < 0$

$(\Delta S)_{U,V} > 0$

Correct option is (d)

39. $A(s) \rightarrow A(\ell)$ $\Delta G = 200\ Jmol^{-1}$

$\Delta V_m = -2 \times 10^{-6} m^3 mol^{-1}$

$\Delta G_2 - \Delta G_1 = \Delta V_m (P_2 - P_1)$ $P_1 = 1\ bar = 10^5\ Pa$

For reaction to be spontaneous $\Delta G < 0$

or to find minimum pressure at which reaction become spontaneous, we can put $\Delta G = 0$

$\Rightarrow \Delta G_2 - \Delta G_1 = \Delta V_m (P_2 - P_1)$

$\Rightarrow 0 - 200 = -2 \times 10^6 (P_2 - 10^5)$ $\Rightarrow 10^8 = P_2 - 10^5$

$\Rightarrow P_2 = 10^5 + 10^8$ $\Rightarrow P_2 = 10^5 (1 + 1000)\ Pa$

$\Rightarrow P_2 = 1001 \times 10^5\ Pa = 1001\ bar$

Correct answer is (1001)

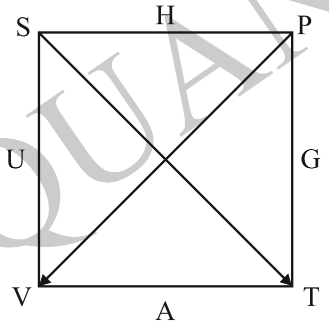
40. $dG = -SdT + VdP$ $dA = -SdT - PdV$

$\left(\frac{\partial G}{\partial T}\right)_P = -S$ $\left(\frac{\partial A}{\partial T}\right)_V = -S$

Correct option is (a)

GATE 2017

41.



$\left(\frac{\partial P}{\partial S}\right)_v = -\left(\frac{\partial T}{\partial V}\right)_S$

Correct option is (c)

42. $Sn(s) + Pb^{2+} \rightleftharpoons Sn^{2+} + Pb(s)$; $n = 2$

$\Delta G^0 = nf E^0$

$$E^0 = \frac{2700}{2\times 96500} = 0.0139$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$0.0139 = -0.126 - E^0_{anode}$$

$$\boxed{E^0_{anode} = -0.1399 \approx 0.14V}$$

Correct answer is (–0.14)

43. $n_{He} = 1$ mol $\quad n_{Ne} = 3$ moles $\quad n_{An} = 2$ moles

$$\Delta G_{mix} = nRT\Sigma x_1 \ell n x_1$$

$$\frac{\Delta G_{mix}}{RT} = n\Sigma x_i \ell n x_i = 6\left\{\frac{1}{6}\ell n\frac{1}{6} + \frac{3}{6}\ell n\frac{3}{6} + \frac{2}{6}\ell n\frac{2}{6}\right\}$$

$$= 6\{-0.2986 - 0.3465 - 0.3662\} = 6.067 = 6.07$$

Correct answer is (6.07)

GATE 2018

44. $$\Delta S_{mix} = -nr\sum x_i \ell n x_i$$

$$= -4\times 8.314\left\{\frac{1}{2}\ell n\frac{1}{2} + \frac{1}{2} + \frac{1}{2}\ell n\frac{1}{2}\right\}$$

$$= -4\times 8.314\times 2\times\frac{1}{2}\ell n\frac{1}{2} = 23.05\ JK^{-1}$$

Correct answer is (23.05 JK^{-1})

45. $T_1 = 298$ K; $T_2 = 400$ K

$C_{p,m} = (14 + bT)\ JK^{-1}\ mol^{-1}$

$$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} nC_{p,m}dT$$

$$\Delta H = \int_{H_1}^{H_2}(14 + bT)dT \Rightarrow \Delta H = 14\ (T_2 - T_1) + \frac{b}{2}\left\{T_2^2 - T_1^2\right\}$$

$$= 14\ (350 - 300) + \frac{b}{2}\{350^2 - 300^2\}$$

$$2000 = 700 + \frac{32500b}{2} \Rightarrow 1300 = \frac{32500b}{2}$$

$b = 0.08\ Jk^{-2}\ mol^{-1}$

GATE 2019

46. Sol. $\Delta H_f = 80 \text{cal } g^{-1}, \Delta S = 28.80 \text{cal } K^{-1}$ for x mole,

$$\Delta H = T\Delta S - 28.80 \times 273$$

$$\Delta H = 7862.4 \text{cal}$$

Amount of water in gm undergo fusion will be,

$$\frac{7862.4 \text{cal}}{80 \text{cal } g^{-1}} = 98.28 g$$

$\Rightarrow$ mole of water undergo fusion will be,

$$x = \frac{98.28}{18} = 5.46$$

47.Sol. $P_1 = 12$ atm, $V_1 = V$

$P_2 = 2$ atm, $V_2 = 3L$

$W = -P_2 (V_2 - V_1)$

$= -2\left(3 - \frac{1}{2}\right) L \text{ atm}$

$= -2 \times \frac{5}{2} L \text{ atm}$

$= -\frac{5L \text{ atm} \times 2 \text{cal mol}^{-1} k^{-1}}{0.082 \text{ L atm mol}^{-1} k^{-1}}$

$= -121.95$ Ca L

$P_1V_1 = P_2V_2$

$12V = 3 \times 2$

$V = \frac{6}{12} L$

$V = \frac{1}{2} L$

48.Sol. $SO_2(g) + \frac{1}{2}O_2 \rightleftharpoons SO_3(g)$

$$\Delta G_f^o (SO_2) = -300 \text{ kJ mol}^{-1}, \Delta G_f^o (SO_3) = -371 \text{ kJ mol}^{-1}$$

$$\Delta G_{rxn}^o = -371 - (-300) - \frac{1}{2}(0)$$

$$= -71 \text{ kJ mol}^{-1}$$

as we know, $\Delta G^o = -RT \ln K_p$

$-71000 = -8.31 \times 298 \ln K_p$

$\ln K_p = 28.67$

$K_p = 283 \times 10^{10}$

GATE 2020

49.Sol.: $\Delta S_{mix} = -R\left[\sum n_i \ln x_i\right]$

$$= -8.314\left[3\ln\frac{3}{4} + 1\ln\frac{1}{4}\right]$$

$$= -8.314\left[3\ln 0.75 + 1\ln 0.25\right]$$

$$= -8.314\left[-0.863 + (-1.386)\right]$$

$$= 18.69 \text{ JK}^{-1}$$

50.Sol.: $\Delta G_f^o(T_2) = T_2\left[\frac{\Delta G_f^o(T_1)}{T_1} + \Delta H_f^o(T_1) \times \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$

$$= 400.\text{K} \times \left[\frac{370.7 \times 10^3 \text{ J mol}^{-1}}{298.15\text{K}} + 416.3 \times 10^3 \text{ J mol}^{-1} \times \left(\frac{1}{400.\text{K}} - \frac{1}{298.15\text{K}}\right)\right]$$

$$\Delta G_f^o(400.\text{K}) = 355.1 \text{ kJ mol}^{-1}$$

51.Sol.: For one mole of the gas, the van der Waals equation is

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

or $$pV_m - pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT$$

To the first approximation V_m in the correction terms may be replaced by RT/p. Thus, we have

$$pV_m - pb + \frac{ap}{RT} - \frac{abp^2}{(RT)^2} = RT \text{ or } V_m = \frac{RT}{p} + b - \frac{a}{RT} + \frac{abp}{(RT)^2}$$

Now $$V_{m,\text{ ideal}} - V_{m,\text{ real}} = -\left(b - \frac{a}{RT} + \frac{apb}{(RT)^2}\right)$$

Since

$$\ln\frac{f}{p} = -\frac{1}{RT}\int_0^p \left(V_{m,\text{ideal}} - V_{m,\text{real}}\right)dp$$

we get $$\ln\frac{f}{p} = \frac{1}{RT}\int_0^p \left(b - \frac{a}{RT} + \frac{abp}{(RT)^2}\right)dp = \frac{1}{RT}\left(bp - \frac{ap}{RT} + \frac{abp^2}{2(RT)^2}\right) \quad \text{... (1)}$$

$$\ln\frac{f}{p}=\frac{bp}{RT}-\frac{ap}{(RT)^2}+\frac{abp^2}{2(RT)^3}$$

$$\frac{bp}{RT}=\frac{\left(0.0399\text{ L mol}^{-1}\right)\left(95\text{ atm}\right)}{\left(0.0821\text{ L atm K}^{+}\text{mol}^{-1}\right)\left(308\text{ K}\right)}=0.15$$

$$\frac{ap}{(RT)^2}=\frac{\left(1.49\text{ L}^2\text{atm mol}^{-2}\right)\left(95\text{ atm}\right)}{\left[\left(0.0821\text{ L atm K}^{+}\text{ mol}^{-1}\right)\left(308\text{ K}\right)\right]^2}=0.22$$

$$\frac{abp^2}{2(RT)^3}=\frac{\left(1.49\text{ L}^2\text{ atm mol}^{-2}\right)\left(0.0349\text{ L mol}^{-1}\right)\left(95\text{ atm}\right)^2}{2\left(0.0821\text{ L atm K}^{-1}\text{ mol}^{-1}\cdot 308\text{ K}\right)}=1.7\times10^{-4}$$

$$\Rightarrow \ln\frac{f}{p}=0.15-0.22+0.00017=-0.07$$

$$\frac{f}{p}=0.93$$

$f = 0.93$ (95 atm)

$f = 88.47$ atm

GATE 2021

52.Sol. Efficiency of heat engine $\frac{T_h-T_c}{T_h}\times100$

$$=\frac{500-400}{500}\times100$$

$= 20$

53.Sol. Since work done on the gas asked

$W = p_{ext} = (V_2 - V_1)$

= 1 atm (3.5 - 2)L

= 1.5 atm × L (1 atm L = 100)

= 1.5 × 100 Joule

= 150 Joule

54.Sol. $2P_{(s)} + 3Br_2(I) \rightarrow 2PBr_3(l)$

$\Delta H_{reaction} = -243$ kJ

for per mole of P, $\Delta H_{reaction} = -\frac{243}{2}\text{ kJ / mol}$

$$\text{for 3.1 g of phosphorus } = \frac{3.1\,\text{g}}{31\,\text{g}/\text{mol}} = 0.1\,\text{mol}$$

$$\text{the enthalpy change } = -\frac{243}{2} \times 0.1$$

= – 12.15 kJ

QUANTA CHEMISTRY CLASSES
An institute of Chemical Sciences

3

STATISTICAL THERMO

GATE 2005

1. (1) Many electron 'wave function' → slater determinats
(2) Low temperature → adiabatic demagenetization
(3) Means speed → maxwell distribution
(4) Nuclear ensemble → partition function
Correct option is (b)

2. Vibration partition function

$$q_{vib} = \frac{e^{-\frac{hv}{2k_BT}}}{\left(1-e^{-\frac{hv}{k_BT}}\right)}$$

Correct option is (d)

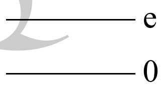
3. $$(u_{av})_{H_2} = \sqrt{\frac{8RT}{\pi M_{H_2}}} \qquad (u_{av})_{D_2} = \sqrt{\frac{8RT}{\pi M_{D_2}}}$$

$$\frac{(u_{av})_{D_2}}{(u_{av})_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{D_2}}} = \sqrt{\frac{2}{4}} = \frac{1}{\sqrt{2}}; (u_{av})D_2 = \frac{1.78}{1.41} = 1.26\ kms^{-1}$$

Correct option is (a)

GATE 2006

4.



$$q = e^{-0/k_BT} + e^{-\varepsilon/k_BT} = 1 + e^{-\varepsilon/k_BT} = 1 + e^{-\varepsilon/k_B(\infty)} = 1 + 1 = 2$$

Correct option is (c)

GATE 2007

$$q \propto \frac{1}{\sigma.\frac{1}{I}} \Rightarrow \boxed{q \propto \frac{I}{\sigma}} \quad ...(1)$$

$$\text{For } H_2, I = \frac{m_1 m_2}{m_1 + m_2}; I = \frac{1}{2}, \sigma = 2 \text{ (Homonulear diatomic molecule)}$$

$$\text{For HD}, I = \frac{1\times 2}{1+2} = \frac{2}{3}, \sigma = 1 \text{ (Heteronuclear diatomic molecule)}$$

$$\frac{q_{H_2}}{q_{HD}} = \frac{\left(\frac{I_{H_2}}{\sigma_{H_2}}\right)}{\left(\frac{I_{HD}}{\sigma_{HD}}\right)} = \frac{\frac{\frac{1}{2}}{2}}{\frac{\frac{2}{3}}{1}} = \frac{1\times 3}{4\times 2} = \frac{3}{8}$$

Correct option is (a)

6. $\varepsilon_0 = \varepsilon_1 = 1.38 \times 10^{-21}$ J and $\varepsilon_2 = 2.76 \times 10^{-21}$ J

$T = 100$ K, $E_{total} = U = \Sigma n_i \varepsilon_i = 1.38 \times 10^{-18}$ J

We know

$U = \Sigma n_i \varepsilon_i$

$$U = n_0\varepsilon_0 + n_1\varepsilon_1 + n_2\varepsilon_2 = \frac{N}{q} e^{-\beta\varepsilon_0} \cdot \varepsilon_0 + \frac{N}{q} e^{-\beta\varepsilon_1} \cdot \varepsilon_1 + \frac{N}{q} e^{-\beta\varepsilon_2} \cdot \varepsilon_2$$

$$= \frac{N}{q}\left\{e^{-\beta\varepsilon_0} \cdot \varepsilon_0 + e^{-\beta\varepsilon_1}\varepsilon_1 + e^{-\beta\varepsilon_2} \cdot \varepsilon_2\right\} \quad ...(1)$$

$$= \frac{N}{q}\left\{\varepsilon_0 e^{-\beta\varepsilon_0} + \varepsilon_0 e^{-\beta\varepsilon_0} + 2\varepsilon_0 e^{-\beta\varepsilon_0}\right\} = \frac{N}{q} \frac{\left\{e^{-\beta\varepsilon_0} + e^{-\beta\varepsilon_0} + 2e^{-\beta\varepsilon_0}\right\}\varepsilon_0}{q} = \frac{N}{q} \times q \times \varepsilon_0$$

$U = N\varepsilon_0$

$$1.38 \times 10^{-18} = N \times 1.38 \times 10^{-21}; \; N = \frac{1.38\times 10^{-18}}{1.38\times 10^{-21}}$$

$$\boxed{N = 1000}$$

Correct option is(a)

GATE 2008

7. At T = 300 k

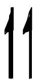
$$\text{Thermal energy} = k_B T = 1.38 \times 10^{23} \frac{J}{k} \; 300 \text{ k}$$

$= 1.38 \times 10^{-21} \times \mathrm{J} = \dfrac{3\times1.38\times10^{-21}\,\mathrm{cm}}{hc}$

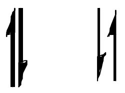
$= \dfrac{3\times1.38\times10^{-21}}{6.63\times10^{-34}\times3\times10^{10}}\,\mathrm{cm}^{-1} = \dfrac{3\times1.38\times10^{3}}{6.63\times3} = \dfrac{4.14\times10^{3}}{1989} = 208$

Correct option is (d)

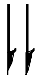
8. Two non-identical spin-½ particles total orientation



(1)



(2)



(3)

Correct option is (d)

9. Total valume = V

Probability to be in $\dfrac{V}{2}$ volume $= \left(\dfrac{V/2}{V}\right) = \dfrac{1}{2}$

For N number of particles,

Probability that all N particle will be found in $\dfrac{V}{2}$ volume $= \left(\dfrac{V/2}{2}\right)^{N} = \left(\dfrac{1}{2}\right)^{N}$

Correct option is (c)

10. Let total molecules = 100

i is the ground state and *j* is excited state

$n_i = 85,\ g_i = 1;\ n_j = 15,\ g_j = 2$

$\Delta\overline{v} = 360\ \mathrm{cm}^{-1},\ \Delta\varepsilon = hc\Delta\overline{v}$

$\Delta\varepsilon = 6.626\times10^{-34}\times3\times10^{10}\times360;\ \ \Delta\varepsilon = 7.156\times10^{-20}$

We know that,

$$\frac{n_j}{n_i} = \frac{g_j}{g_i}e^{-\frac{\Delta\varepsilon}{k_BT}} \Rightarrow \frac{15}{85} = \frac{2}{1}e^{-\frac{7.156\times10^{-20}}{1.38\times10^{-23}\cdot T}} \Rightarrow \boxed{T = 200K}$$

Correct option is (c)

GATE 2012

11. $q(T) = \left(\dfrac{k_BT}{hc}\right)\left(\dfrac{8\pi^2mk_BT}{h^2}\right)^{3/2}$

$$q \propto T^{3/2} \cdot T^{3/2} \Rightarrow q \propto T^3$$

$$C_P = \left(\frac{\partial U}{\partial T}\right)_V \Rightarrow U = NkT^2\left(\frac{\partial \text{In } q}{\partial t}\right)_V$$

$$\text{Inq} \propto \text{In } T^3 \Rightarrow \text{In } q \propto 3 \text{ In } T$$

$$\frac{\partial}{\partial T}(\text{In } q) \propto \frac{3\partial}{\partial T}\text{In } T \Rightarrow \left(\frac{\partial \text{ In } q}{\partial T}\right) \propto \frac{3}{T} \Rightarrow U = NkT^2\left(\frac{3}{T}\right) \Rightarrow U = 3NkT$$

$$C_P = \left(\frac{\partial U}{\partial T}\right)_V = 3NK \Rightarrow C_P = 3N_Ak \Rightarrow \boxed{C_P = 3R}$$

Correct option is (a)

GATE 2014

12. $$\frac{n_J}{\eta_0} = e^{-\frac{\Delta E}{K_BT}} \Rightarrow 9.22\times10^6 = e^{-\frac{\Delta E}{1.38\times10^{-23}\frac{J}{K}\times300K}}$$

$$\text{In } 9.22\times10^6 = \frac{-\Delta E}{1.38\times10^{-23}\times300\text{ J}} \Rightarrow 2.22+13.81=\frac{-\Delta E}{1.38\times10^{25}\times3\text{ J}}$$

$16.03 \times 1.38 \times 10^{-25} \times 3 \text{ J} \times 6.023 \times 10^{23} = -\Delta E$

399.8×10^2 J = 39.98 KJ/mole

Correct answer is (39.98)

GATE 2015

13. For an ideal gas with molar mass M, molar translational entropy.

$S \propto \ell nM$

Correct option is (d)

14. $q_{rot} = g_0e^{-(J+1)\varepsilon} + g_1e^{-(J+1)\varepsilon}$; $J = 0 = 1\ e^{-0}$

$g_0 = (2J + 1)J = 0$; $g_0 = 1$

$J = 1 = 3e^{-2\varepsilon}$; $g_1 = (2J + 1)$ $J = 1 = 3$; $g_1 = 3$

Correct option is (b)

GATE 2016

15. $$\frac{n_J}{\eta_0} = \frac{g_J}{g_0}\ e^{-[E_J-E_0]/K_BT}\ ;\ g_J = g_0;\ \frac{n_J}{\eta_0} = 1\ e^{\frac{0.1eV}{0.05eV}}\ ;\ \frac{n_J}{\eta_0} = e^{-\left(\frac{0.1eV}{0.05eV}\right)}$$

$$\frac{n_J}{\eta_0} = e^{-(2)};\ \ell n\frac{n_J}{\eta_0} = -(2)$$

$$2.303 \log \frac{n_J}{\eta_0} = -2; \quad \log \frac{n_J}{\eta_0} = \frac{-2}{2.303}; \ \log \frac{n_J}{\eta_0} = -0.8684; \left\{\frac{n_J}{\eta_0} = 0.14\right\}$$

Correct answer is (0.14)

GATE 2017

16. For canonical ensemble → N, V, T = constant

NVT	NVT	NVT
NVT	NVT	NVT
NVT	NVT	NVT

Correct option is (a)

GATE 2019

17. Sol. Partition Function, $q = \Sigma g_1 e^{-\varepsilon_1/KT}$

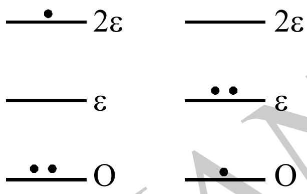
$$q = g_0 e^{-E_0/KT} + g_1 e^{-E_1/KT}$$

$$= 1e^{-0/KT} + 2e^{-\frac{2KT}{KT}}$$

$$= 1 + 2e^{-2}$$

$$q = 1.27$$

18.Sol.



$W_1 = \frac{3!}{1! \times 2!}$ $W_2 = \frac{3!}{2! \times 1!}$

$= 3$ $= 3$

Total ways, $W = W_1 + W_2$

$W = 3 + 3 = 6$

4

EQUILIBRIA

GATE 2005

1. The triple point for water is uniqe ⇒ fixed

   $T = 0.01°C, P = 4.58\ mmHg$

   Correct option is (a)

2. $H_2O\ (liquid) \rightleftharpoons +120\ (gas)$

   $\mu(T, P) = \mu^0\ (T) + RT\ In\ P$

   Change in chemical potential

   $\Rightarrow\ \mu(T, P) - \mu^0\ (T) = RT\ In\ P/P0$

   $\Rightarrow\ \Delta\mu = 8.314\ J\ mol^{-1}\ K^{-1} \times 298\ K \times In\left(\frac{24}{1}\right)$

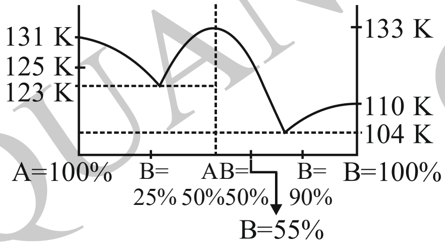
   $\Rightarrow\ \Delta\mu\ 8.314 \times 298 \times In\ 24\ Jmol^{-1}$

   $\Rightarrow\ \Delta\mu = 7873.8\ mol^{-1}\ K^{-1}$

   $\Rightarrow\ \Delta\mu = 7.87\ kJ\ mol^{-1}$

   Correct option is (c)

GATE 2006

3. 

   At point a, AB(s) + Melt.

   Correct option is (b)

4. On adding solid B, it will precipitate out.

   Correct option is (b)

5. On cooling mixture at 25 mole percent B to 114 K. Solid AB + solid A will exist.

   Correct option is (a)

GATE 2007

6. $V_{solution} = 100$ mL $[HA] = 1.2$ A $[NaA] = \gamma M$

The given solution is buffer solution

$n_{HA} = 1.2 \times 100 = 120$ m mol

$nH_{aA} = y \times 100 = 100y$ mmol

On adding NaOH = 40 mmol,

	HA	$+ NaOH \longrightarrow$	NaA	$+ H_2O$
Initial amount	120	40	0	0
After reaction	120–40 = 80	0	40	

In solution, $n_{HA} = 80$ mmol; $mN_{aA} = (100y + 40)$ mmol

$$pH = pK_a + \log \frac{n_{salt}}{n_{acid}};\ 5.3 = 5 + \log \frac{100y + 40}{80}$$

$$0.3 = \log \frac{100y + 40}{80} \Rightarrow 2 = \frac{100y + 40}{80} \Rightarrow y = \frac{120}{100} = 1.2\ M$$

In the beginning $n_{NaA} = 100y = 100 \times 1.2 = 120$ mm

$$pH = pK_a + \log \frac{n_{salt}}{n_{acid}} = 5 + \log \frac{120}{120}$$

$\boxed{pH = 5}$

Correct option is (b)

7. $NaCl \rightleftharpoons Na^+ + Cl^{-1}$

$C = 2 - 1 = 1$

$F = C - P + 2$

$F = 2 - 2 + 2 = 2$

Therefore, F = 2

Correct option is (a)

GATE 2008

8. Maximum number of phase that can exist in equilibrium is 3.

Correct option is (a)

GATE 2009

9. $Sucrose(s) \rightleftharpoons Sucrose\ (aq)$

It is a non-reactive system.

Therefore, C = number of chemical constitute which is 2 here C = 2.

Correct option is (c)

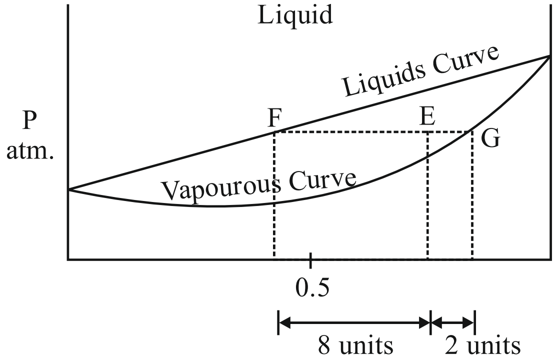
10. When $\Delta ng = 0$ then pressure has no effect on equilibrium.

In option (d); $\Delta ng = 4 - 4 = 0$

Correct option is (d)

11. $$\frac{\text{Amt. of liquid at E}}{\text{Amt. of vapour at E}} = \frac{EG}{FE}$$

$$\frac{\text{Amt. of liquid at E}}{\text{Amt. of vapour at E}} = \frac{2}{8} = \frac{1}{4}$$



$$\frac{\text{Amt. of liquid at E}}{\text{Amt. of vapour at E}} = +1 = \frac{1}{4} + 1$$

$$\frac{\text{Amt. of liquid at} + \text{Amt. of vapour}}{\text{Amt. of vapour}} = \frac{5}{4}$$

$$\Rightarrow \frac{\text{Amt. of vapour}}{\text{Amt. of liquid} + \text{Amt. of vapour}} = \frac{5}{4} \Rightarrow x_B \text{ in vapour form} = 0.8.$$

correct option is (d)

GATE 2010

12. Possible number of triple points is 4

Three are stable triple point and one is metastable triple point.

Correct option is (d).

13. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ k_{p1}

$\frac{1}{2}N_2(g) + \frac{3}{2}H2(g) \rightleftharpoons NH_3(g)$ l_{p2}

$$k_{p1} = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3}; k_{p_2} = \frac{[P_{NH_3}]}{[P_{N_2}]^{½}[P_{H_2}]^{3/2}} = \left[\frac{[PNH_3]^2}{[P_{N_2}][P_{H_2}]^2}\right]$$

Correct option is (c)

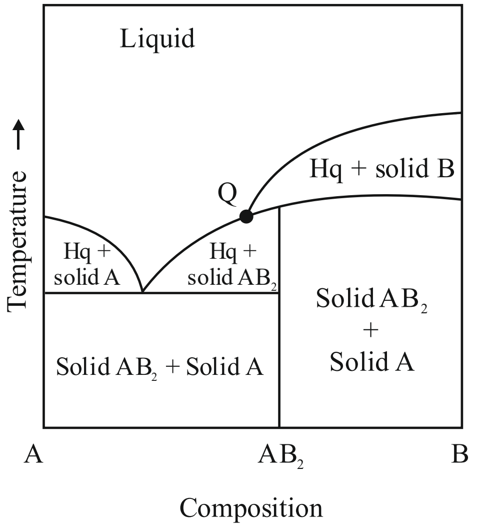
GATE 2011

14. **Tripl**e point is the piont on the P – T diagram for one compnent systement at which the solid-liquid and the liquid gas curves intersect. At this point all three phases (solid and vapour) can co-exist in equilibrium.

Correct option is (a)

GATE 2012

15.



So, at point Q. Solid AB_2, B and liquid are in equilibrium
Correcrt option is (c)

GATE 2014

16. $H_2O(s) \rightleftharpoons H_2O(\ell)$ $\Delta H_{fus} = 6.01\ kJ\ mol^{-1}$

$H_2O(s) \rightleftharpoons H_2O(g)$ $\Delta H_{avp} = 44.83\ kJ\ mol^{-1}$

$H_2O(s) \rightleftharpoons H_2O(g)$ $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$

$= 6.01 + 44.83$

$\Delta H_{sub} = 50.84\ kJ\ mol^{-1}$

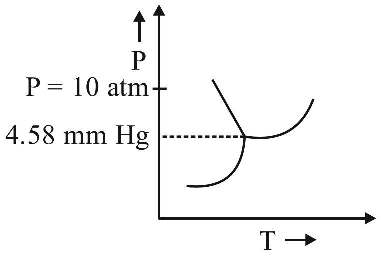
Correct option is (50.84)

GATE 2016

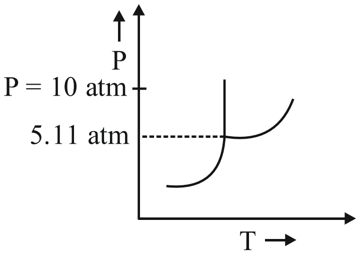
17. At R the liquid is pure X
Correct option is (d)

GATE 2017

18.



H_2O phase diagram



CO_2 phase diagram

Slope of HO wil be negative for s-l equilibrium line

Slope CO is positive for s-l equilibrium line

$\Rightarrow M_1 < 0$ and $M_2 > 0$

Correct option is (d)

GATE 2018

19. $\Delta H_{vap} = 15300\ Jmol^{-1}\quad T = 200K$

$V_{\ell} = 100\ cm^3\ mol^{-1} = 110 \times 10^{-6}\ m^3mol^{-1}$

$V_g = 12000\ cm^3mol^{-1} = 12000 / 10^{-6}\ m^3\ mol^{-1}$

$$\frac{dP}{dP} = ??\ kP_a k^{-1};\ \frac{dP}{dP} = \frac{\Delta HH_{vap}}{T\Delta V}$$

$$\frac{dP}{dP} = \frac{15300}{200(12000\times10^{-6}\times110\times10^{-6})} = \frac{15300}{200\times11890\times10^{-6}}\left(\frac{Jmol^{-1}}{km^3mol^{-1}}\right)$$

$= 0.0064339 \times 10^6 = 6433.9\ P_aK^{-1} = 6.4339\ kP_aK^{-1}$

GATE 2019

20.Sol. (a) is incorrect

At 200 K, along sublimation curve, solid $\rightleftharpoons$ gas.

On increasing pressure, CO_2 gas gets converted to solid.

GATE 2021

21Sol. $NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$

$\Delta G^o = -RT\ lnkp$

$$k_p = e^{\left(\frac{\Delta G^o}{-RT}\right)}$$

$$k_p = \exp\left(\frac{-104.18\times10^3\,J}{-8.314\times298\,k}\right)$$

$k_p = 1.8 \times 10^{18}$

Correct option is (a)

22Sol. $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

t = 0 0.7 1.0

$t = +_{eq}$ 0.7-P 1.0-P P

here P = 0.15 (equilibrium presence of $CoCl_2$)

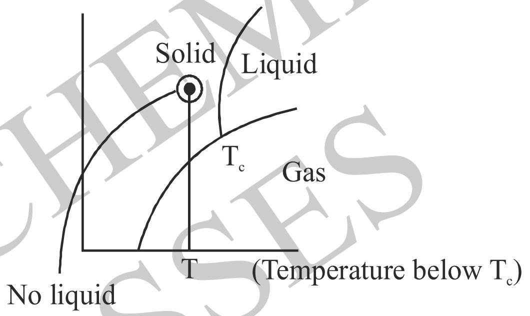
PCO = 0.7 – 0.15 = 0.55

PCl_2 = 1 – 0.15 = 0.85

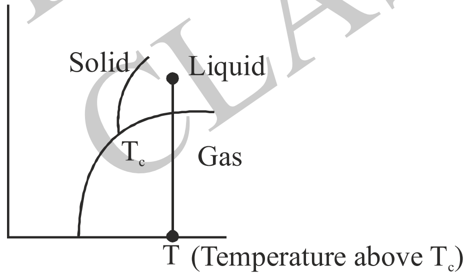
$$k_p = \frac{PCoCl_2}{PCo\times PCl_2} = \frac{0.15}{0.55\times0.85} = 0.32\ bar^{-1}$$

23.Sol. At T_c all hence phases CO exist so ***** is correct.

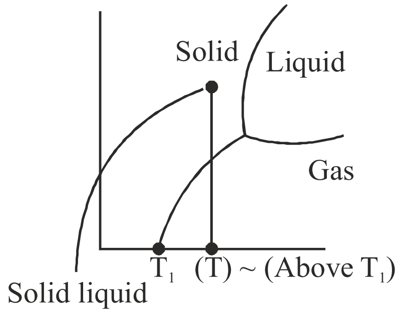
Below T_c liquid state does not exist



Above T_c liquid state exist



Above T_1 solid exist



So, correct option are (a) and (b)

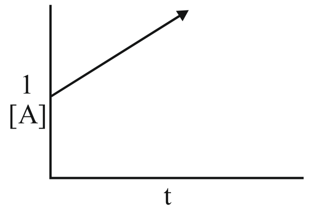
5

KINETICS

GATE 2005

1. Rate law $\Rightarrow -\frac{d[A]}{dt} = k[A]^2$

Reactivity is second order. So, graphically representing.



Correct option is (b)

2. $\phi = \frac{\text{Amt. of sample dissociated}}{\text{Amount of photons absorb}}$

Energy of 1 mol of photon $= \frac{11.97}{\lambda(\text{cm})} \text{Jmol}^{-1} = \frac{11.97}{300\times10^7} = 3.99 \times 10^5$ J mol^{-1}

3.99×10^5 J $\rightarrow$ 1 mol of photon

$6.626 \text{ J} \rightarrow \frac{1\times6.626}{3.99\times10^5} = 1.66 \times 10^{-5}$ mol

$\phi = \frac{10^{-3}}{1.66\times10^{-5}} = 0.6024 \times 10^2$

$\phi = 60.24$

Correct option is (c)

GATE 2006

3. $A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} I + \text{Heat}$

On increasing the temperature, reaction moves backward.

$\Rightarrow$ The magnitude of increase is more for K_{-1} than K_1

$\therefore \dfrac{K_1}{K_{-1}}$ decreases

Correct option is (c).

4. $[^{90}Sr]_0 = 1g$

$[^{90}Sr] = 0.953$ g, t = 2 year

$$k = \frac{2.303}{2}\log\frac{1}{0.953} = 0.024075;\ \boxed{k = 0.024075\ \text{year}^{-1}}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.024075} = 28.785\ \text{year}$$

$t_{1/2} = 28.75$ year

After 5 years amount of ^{90}Sr.

$$0.024075 = \frac{2.303}{5}\log\frac{1}{[Sr]} \Rightarrow \boxed{\left[{}^{90}Sr\right] = 0.887\ g}$$

Correct option is (c)

5. $A \xrightarrow{K_a} B \xrightarrow{K_b} C$

t = 0	a	0	0
t = t	x	y	z

a = x + y + z

$$\frac{-d[A]_t}{dt} = K_a[A] \Rightarrow \frac{-dx}{dt} = K_a x \Rightarrow \int_{x=a}^{x}\frac{dx}{x} = \int_0^t K_a dt \Rightarrow -\text{In}\left(\frac{x}{a}\right) = K_a t$$

$$\text{In}\frac{x}{a} = -K_a t \Rightarrow \frac{x}{a} = e^{-k_a t} \Rightarrow x = a\cdot e^{-K_a t}$$

or $[A] = [A]_0\, e^{-k_a t}$

Correct option is (a)

6. $A \xrightarrow{K_a} B$ (fast) {$K_a >> K_b$ given}

$B \xrightarrow{K_b} C$ (slow)

⇒ The net effect on [B] is the accumulation or increases to some maximum value and then it starts decreasing.

correct option is (b)

GATE 2007

7. Catalyst not affect the activation energy of the reaction.

Correct option is (d)

8. Rate constant = 38 $dm^3\ mol^{-1}\ s^{-1}$

Unit = $dm^3\ mol^{-1}\ s^{-1}$ is second order

Correct option is (c)

9. From experiment (1) and (2), concentration of P is double and rate increase in four times. So, order is 2 with respect to P.

From experiment (2) and (3), concentration of Q is fourth and rate is four times. So, order is 1 with respet ot Q.

$$\frac{r_2}{r_1} = \left(\frac{c_2}{c_1}\right)_P^{\ell} \left(\frac{c_2}{c_1}\right)_Q^{m} \left(\frac{c_2}{c_1}\right)_R^{n}$$

Experiment (1) and (4),

$$\frac{4\times10^{-5}}{4\times10^{-5}} = \left(\frac{0.1}{0.2}\right)^2 \left(\frac{0.25}{0.50}\right)^1 = \left(\frac{1.6}{40}\right)^n \quad \Rightarrow \quad \frac{1}{2} = \frac{1}{4}\times\frac{1}{2}(4)^n \Rightarrow (4)^1 = (4)^n \Rightarrow n = 1$$

Correct option is (c)

10. $t_{1/2} = 28.4$ min

$$K = \frac{0.693}{t_{1/2}} = 0.0244\ \text{min}^{-1}$$

$$[A]_0 = 8\ \text{nM};\ [A] = 1.0\ \text{nM};\ \text{In}\frac{[A]_0}{[A]} = Kt;\ t = 85.2\ \text{min}$$

Correct option is (c)

11. $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

Mechanism :

$$NO + NO \xrightarrow{K_a} N_2O_4;\ N_2O_2 \xrightarrow{K_a'} NO + NO;\ N_2O_2 + O_2 \xrightarrow{K_b} NO_2 + NO_2$$

$r = K_b\,[N_2O_2]\,[O_2]$

Applying SSA on $[N_2O_4]$

Rate of formation = Rate of consumption

$$Ka\,[NO]^2 = K'_a\,[N_2O_4] + K_b\,[N_2O_2]\,[O_2]$$

$$[N_2O_4] = \frac{K_a[NO]^2}{K_a + K_b[O_2]} \Rightarrow r = \frac{K_b[O_2]\cdot K_a[NO]^2}{K_a + K_b[O_2]}$$

Correct option is (b)

12. E2 > E1

$\Rightarrow$ At same temperature $K_2 < K_1$

On increasing the temperature K_2 increase more compared to K_1

$$\text{So, } \frac{K_1(T_2)}{K_1(T_1)} < \frac{K_2(T_2)}{K_2(T_1)}$$

Correct option is (d)

GATE 2008

13. $2X_3 \longrightarrow 3X_2$

$$\text{Rate of formation of } X_2 = \frac{d[X_2]}{dt}$$

Rate of Rection is, $-\frac{1}{2}\frac{d[X_3]}{dt}=\frac{1}{3}\frac{d[X_2]}{dt}\Rightarrow\frac{d[X_2]}{dt}=\frac{-3}{2}\frac{d[X_3]}{dt}$

Correct option is (d)

14. $\text{TOF}=\frac{\text{product}}{\text{catalyst}}\times\frac{1}{\text{time}}=\frac{10^{-3}}{10^{-6}}\times\frac{1}{10}=100$

Correct option is (b)

15. $A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B$

$$\tau=\frac{1}{K_1+K_{-1}}=10^{-6}$$

$\Rightarrow K_1 + K_{-1} = 106$ ...(i)

$A \rightleftharpoons B$

I.C	$[A]_0$	O
E.C	$0.1[A]_{30}$	$0.9[A]_0$

$K_{eq}=\frac{0.9[A]_0}{0.1[A]_0}=9 \quad \Rightarrow \frac{K_1}{K_{-1}}=9$

or $K_1 = 9\,K_{-1}$

Substituting it in equation (i)

$9K_{-1} + K_{-1} = 10^6$

$K_{-1} = 10^5$

Hence, $K_1 = 9 \times 10^5\ s^{-1}$

Correct option is (a)

16. $E+S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} [ES]$

$[ES] \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} E+P$

$$\frac{-d[S]}{dt}=\left\{\frac{K_1K_2[S]_0+K_2K_2[P]}{K_1[S]_0+K_{-2}[P]+K_{-1}+K_2}\right\}[E]_0$$

$r_{max}=K_2[E]_0$

If $K_{-1} + K_2 << K_1[S]_0$

then $-\frac{d[S]}{dt}=\left\{\frac{K_1K_2[S]_0+K_2K_{-2}[P]}{K_1[S]_0+K_{-2}[P]}\right\}[E]_0$

Since it is given that small amount of S is converted to P

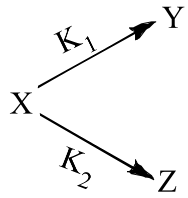
$\Rightarrow K_1[S]_0 >> K_{-2}[P]$ and $K_1K_2[S]_0 >> K_2K_{-2}[P]$

So, $-\frac{d[S]}{dt}=\frac{K_1K_2[S]_0-[E]_0}{K_1[S]_0}\Rightarrow\frac{-d[S]}{dt}=K_2[E]_0=r_{max}$

Correct option is (b)

GATE 2009

17.



$K_1 = 10^{-4}\ s^{-1}$

$$\frac{[Y]}{[Z]} = \frac{1}{4}$$

$$\frac{[Y]}{[Z]} = \frac{K_1}{K_2} = \frac{1}{4};\ K_2 = 4K_1 = 4 \times 10^{-4}\ s^{-1}$$

Correct option is (c)

18. $$t_{1/2} \propto \frac{1}{[A]_0^{n-1}} \Rightarrow \frac{240}{300} = \frac{(4)^{n-1}}{(5)^{n-1}}$$

$$\left(\frac{4}{5}\right)^1 = \left(\frac{4}{5}\right)^{n-1} \Rightarrow n - 1 = 1$$

n = 2 Order of reaction is 2

Correct option is (c)

19. $$\tau = \frac{1}{K_F + K_{ISC} + K_{IC}} = 10 \times 10^{-9}\ \text{sec} \Rightarrow K_F + K_{ISC} + K_{IC} = 10^8\ s^{-1}$$

$$\phi = \frac{K_F}{K_F + K_{ISC} + K_{IC}} = 0.1;\ K_F = 0.1 \times 10^8 = 10^7\ s^{-1}$$

Correct option is (c)

20. $$X + Y \underset{K_2}{\overset{K_1}{\rightleftharpoons}} Z\ (\text{fast})$$

$$Z \xrightarrow{K_3} P\ (\text{slow}) \qquad \text{Since } K_2 >> K_3$$

$$r = K_3[Z];\ \frac{K_1}{K_2} = \frac{[Z]}{[X][Y]}$$

$$\text{or } [Z] = \frac{K_1}{K_2} = [X][Y] \quad \Rightarrow \quad r = \frac{K_3 \cdot K_1}{K_2}[X][Y]$$

Correct option is (a)

21. $$K = Ae^{-E_a/RT}$$

$$\text{In } K = \text{In } A - \frac{E_a}{RT}; K = \frac{K_1K_3}{K_2}$$

$$\text{In K} = \text{In K}_1 + \text{In K}_3 - \text{In K}_2 = \text{In } A_1 - \frac{E_{a_1}}{RT} + \text{In } A_2 - \frac{E_{a_3}}{RT} - \text{In } A_3 + \frac{E_{a_2}}{RT}$$

$$= \text{In}\left(\frac{A_1 \cdot A_2}{A_3}\right)\frac{-1}{RT}\left\{E_{a_1} + E_{a_3} - E_{a_2}\right\}$$

Correct option is (c)

GATE 2010

22. $\text{In k} = 5.0 - \dfrac{12000}{T}$ ...(i)

From Arrhenius equation

$\text{In k} = \text{In A} - \dfrac{E_a}{RT}$ ...(ii)

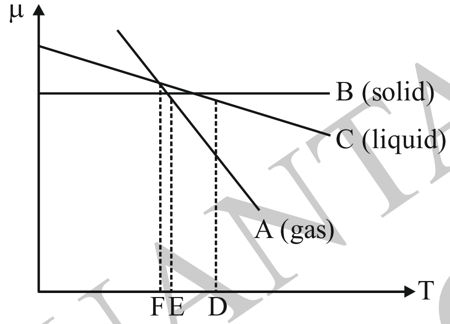
Comparing with two equation, we get

$$-\frac{E_a}{RT} = -\frac{12000}{T}$$

$E_a = 12000 \times 2 = 24.00$ kcl/mol

Correct option is (c)

23.



Correct option is (d)

24. D represnets Melting point

E represents sublimation

F represents boiling point

Correct option is (d)

GATE 2011

25. for first order reaction, $k = \dfrac{2.303}{t}\log\dfrac{a}{a-x}$

$t = 10$ min $\quad a = a,\ a - x = \dfrac{a}{y} \quad \Rightarrow\ k = \dfrac{2.303}{10}\log\dfrac{a}{\frac{a}{4}}$

$$\Rightarrow\ k=\frac{2.303}{10}\log 4 \Rightarrow k=\frac{2.303}{10}\log(2)^2$$

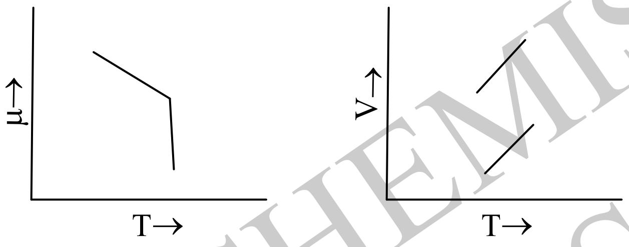
$$\Rightarrow\ k=\frac{2.303\times 2}{1}\log 2 = 0.1386\ \text{min}^{-1}$$

Correct option is (a)

26. $\left(\frac{d_{\mu.\beta}}{dP}\right)_T - \left(\frac{d_{\mu\alpha}}{dP}\right)_P = V_{\beta,m} - V_{\alpha,n} = \Delta_{trs} V$

Accroding to Ehren fest classification a transition for which the first derivative of chemical potential with respect to temperature is discontinuous is classified as First. Order phase transition and volume with respect to termperature is discontinuous is classified as Fist Order phase transition and volume with respect to temperature is discontinuous.

Show first order phase transition $\left(\frac{dU}{dT}\right)_P$ is discontinuous at transfer and $\left(\frac{dV}{dT}\right)_P$ also discontinuous at transition.



Correct option is (b)

27. Given : $K_3[O_3] >> K_2[O_2]\,[M]$; $r=\frac{K_1\cdot K_3[O_3]^2[M]}{K_3[O_2]}$

or $r=\frac{K_1[O_3]^2[M]}{[O_2]}$

$\Rightarrow\ E_a = E_{a_1}$

Correct option is (d)

28. $r = K_3\,[O][O_3]$

Applying SSA on [O]

Rate of formation = Rate of consumption

$K_1[M][O_3] = K_2[O_2][O][M] + K_3[O][O_3]$; $[O]=\frac{K_1[M][O_3]}{K_2[O_2][M]+K_3[O_3]}$

$r = K_3[O_3]$

$R\left\{\frac{K_1[M][O_3]}{K_2[O_2][M]+K_3[O_3]}\right\}$; $r=\frac{K_1\cdot K_3[O_3]^2[M]}{K_2[O_2][M]+K_3[O_3]}$; $r=-\frac{1}{2}\frac{d[O_3]}{dt}$

Rate of decomposition of ozone, $\frac{-d[O_3]}{dt}=2r$

$$\frac{-d[O_3]}{dt} = \frac{2K_1 \cdot K_3[O_3]^2[M]}{K_2[O_2][M] + K_3[O_2]}$$

Correct option is (a)

GATE 2012

29. First step $G \underset{}{\overset{k1}{\rightleftharpoons}} 2H$

Second step, $G + H \xrightarrow{k_1} P$

$$\frac{d[P]}{dT} = k_1^{'}[G][H] \qquad ...(i)$$

From equilibrium constant, $K_c = \frac{[H]^2}{[G]}$

$$k_c^{1/2}[G]^{½} = [H] \Rightarrow \frac{d[P]}{dt} \propto [G]^{3/2}$$

Putting [H] in equation (i)

$$\frac{d[P]}{dt} = k_1 k_c^{½}[G]^{3/2}$$

Correct option is (d)

30. Consider the reaction, $H_2 + C_2H_4 \longrightarrow$ C2H6

$$\left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \left(\frac{8k_BT}{\pi\mu}\right)^{½} N_A$$

The molecular diameter of H_2 and C_2H_4 = 1.8Å and 3.6Å.

The pre exponential factor in the rate constant calculated using collision Theory is (m^3 per mole per sec) is approx. ( ) for this reaction at 300K

$$\left(\frac{8k_BT}{\pi\mu}\right)^{½} N_A = 1.11 \times 10^{27} \text{ m mole}^{-1} \text{ sec}^{-1}$$

$$k_2 = P\left[\underbrace{N_A \pi\sigma_{AB}^2 \left(\frac{8k_BT}{\pi\mu}\right)^{½}}_{\text{pre-exp opential factor}}\right]\frac{e^{-E_a/RT}}{\text{exp onential factor}}$$

$$P = 1 \qquad \Rightarrow k_2 = A\, e^{-E_a/RT}$$

$$k_2 = N_A \pi\sigma_{AB}^2 \left(\frac{8k_BT}{\pi u}\right)^{½} e^{-E_a/kT}$$

$$= 3.1452.y^2 \times 10^{-20} \times 1.11 \times 10^{27}\ m^3\ mol^{-1}\ s^{-1}$$

$$= 25.408 \times 10^{-20} + 27 = 25.408 \times 10^{7}\ m^3\ mol^{-1}\ s^{-1}$$

$k_2 = 2.54 \times 10^{8}\ m^3\ mol^{-1}\ s^{-1}$

Correct option is (a)

GATE 2013

31. According to L.C. principles, On decreasing pressure shifts in the direction in which the number of gaseous molecules increases.

Correct option is (c)

32. The concentration of the component which is present in steady practicaly remains constant except at the very begining and at the very end.

Correct option is (c)

33. $X \underset{K_2}{\overset{K_1}{\rightleftharpoons}} Y$

$$At = t = t\ [X]\ [X]_0 - [X];\ \frac{-d[X]}{dt} = K_1[X] - K_2[Y]$$

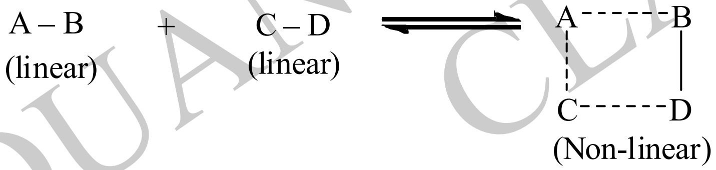
$$\frac{-d[X]}{dt} = K_1[X] - K_2\ \{[X]_0 - [X]\} = K_1[X] + K_2\ [X] - K_2[X]_0$$

$$\frac{-d[X]}{dt} = (K_1 + K_2)\ [X] - K_2\ [X]_0$$

Correct option is (b)

34. $q_{trans} \propto T^{3/2}$ $\quad q_{vib} \propto T^{0}$

$q_{vib} \propto T(\text{linear}),$ $\quad q_{rot} \propto T^{3/2}(\text{Non}-\text{linear})$



Arrhenius pre-exponential factor

$$A = \frac{N_A k_B T}{h} \frac{\left(q_{r(non)} q_{r(non)} q_{vib}\right)_{non-linear}}{\left(q_{r(linear)} q_{rot(linear)} q_{v(linear)}\right)_{(A-B)} \left(q_{r(linear)} \cdot q_{r(linear)} \cdot q_{v(linear)}\right)_{CD}}$$

$$= \frac{N_A k_B T}{h} \frac{T^{3/2} \cdot T^{0}}{\left(T^{3/2} \cdot T \cdot T^{0}\right)\left(T^{3/2} \cdot T \cdot T^{0}\right)} = \frac{N_A k_B T}{h} \cdot \frac{1}{T^2};\ A \propto \frac{1}{T} \Rightarrow \boxed{A \propto T^{-1}}$$

Correct option is (a)

GATE 2015

35. $A = \frac{k_B T}{h} e^{\frac{\Delta S^{\#\#}}{R}} \; e^{-\left(\Delta n_g{}^{\#} - 1\right)} = 2.17 \times 10^{-11} \text{ s}^{-1} = \frac{1.38 \times 10^{-23} \times 298}{6.63 \times 10^{-34}} \times e^{\frac{\Delta S^{\#\#}}{e8.314}} \times e^{1}$

$\Delta S^{\#} = [10.2 - 10.6]$*

Correct option is (c)

GATE 2016

36. Enthalpy of activation,

$\Delta H^{\#} = E_a - 2RT$ [for bi-molecular reaction]

$= 5500 - 2 \times 8.314 \times 300 = 511.6$ J/mole $= 0.5116$ kJ/mole

Correct answer is (5)

37. $A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B$

$K_1 = 4.2 \times 10^{-4} \text{ s}^{-1}$; $K_2 = 1.04 \times 10^{-3} \text{s}^{-1}$

$$\tau = \frac{1}{k_1 + k_{-1}} = \frac{1}{(4.2 \times 10^{-4}) + (1.04 \times 10^{-3})} = 684.93$$

Correct answer is (6.6)

38. $A + B \underset{K_{-1}10^4}{\overset{K_1 = 10^5}{\rightleftharpoons}} I$ (fast)

$I \xrightarrow{K_2 = 10} P$ (slow)

$$\frac{d[P]}{dt} = K_2[I];\ K_{eq} = \frac{K_1}{K_{-1}}[A]\,[B] \Rightarrow \frac{d[P]}{dt} = \frac{K_2.K_1}{K_{-1}}[A]\,[B]$$

So, rate constant of product formation is $\frac{K_2.K_1}{K_{-1}}$

$\frac{10 \times 10^5}{10^4} = 100 \text{ L mol}^{-1}\text{s}^{-1}$

Correct answer is (100)

GATE 2017

39. $K = 1.25 \times 10^{-4}$ mol $L^{-1}s^{-1}$

$[A]_0 = 0.250$

Time for $[A] = 0$

Unit of K shows zero order reaction

$[A]_0 - [A] = Kt$; $[A]_0 = Kt$

$t = \frac{0.250}{1.25\times10^{-4}} = 0.2 \times 10^{-4}$; $t = 2 \times 10^{3}$ sec.

Correct answer is (2000)

40 $\text{In } K = -\frac{5000}{T} + 10$

$\text{In } K = A - \frac{E_a}{RT} \Rightarrow \quad -\frac{E_a}{RT} - \frac{5000}{T}$

$E_a = 5000 \times 8.314$; $E_a = 41570$ J

$E_a = 41.57 \text{ kJmol}^{-1}$

Correct answer is (41.57)

41. $X \xrightarrow{K_1=2s^{-1}} Y \xrightarrow{K_2=0.1s^{-1}} Z$

$$t_{max} = \left(\frac{1}{K_1 - K_2}\right)\ln\left(\frac{K_1}{K_2}\right) = \left(\frac{1}{-0.1}\right)\ln\left(\frac{2}{0.1}\right) = \frac{1}{1.9} \times 2.99$$

$t_{max} = 1.576$ sec

Correct option is (1.576)

42. Rectant + Enzyme → product

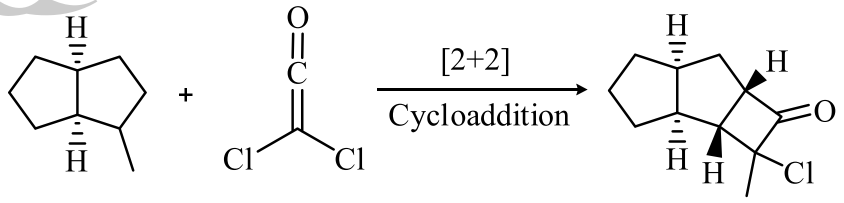
$$\text{Turn over number} = \frac{\text{mole of reactant}}{\text{minimum amount of enzyme} \times \text{required time}}$$

$$= \frac{\left(\frac{0.44}{44}\right)}{\frac{x}{30000}\times100} = 4 \times 10^{5} \Rightarrow x = 7.5 \times 10^{-6}\text{g} = (7.5\ \mu\text{g})$$

Correct answer is (7.5)

GATE 2018

43.



Addition from less hindered face

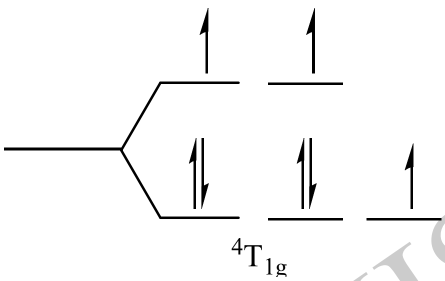
Correct option is (c)

44. $\text{In}\,\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$ $E_a = \Delta H, E_a = 2800\text{ J}$

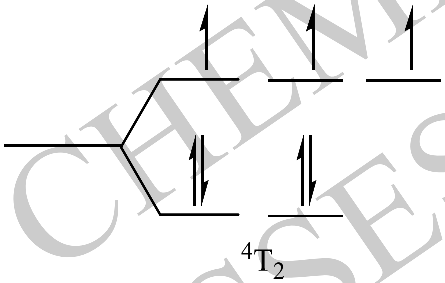
$$\text{In}\,\frac{k_2}{1.6\times10^{-3}} = \frac{2800}{8.314}\left[\frac{1}{300} - \frac{1}{350}\right],\ k_2 = 7.95 \times 10^{-3}$$

$$t = \frac{2.303}{k_2}\log\left|\frac{a}{a-x}\right| = \frac{2.303}{7.9\times10^{-3}}\log\left|\frac{100}{10}\right| = \frac{2.303}{7.95\times10^{-3}}\log 10 = 289.6\text{ sec}$$

45. $[Co(H_2O)_6]^{2+}$ $\Rightarrow$ Co^{2+} d^7 (O_h)



$[CoCl_4]^{2+}$ $\Rightarrow$ Co^{2+} d^7 (Td)



Correct option is (b)

GATE 2019

46.Sol. $A = \frac{k_B T}{h} e^2 . e^{\frac{\Delta S}{R}}$

$$10^{13} = \frac{1.38\times10^{-23}\times298}{6.62\times10^{-34}}.e^2.e^{\frac{\Delta S}{R}}$$

$$e^{\frac{\Delta S}{R}} = \frac{6.62\times10^{-21}}{1.38\times298\times10^{-23}\times7.389}$$

$= 0.002178 \times 10^2$

$= 0.2178$

$$\frac{\Delta S}{R} = -1.524$$

$\Delta S = -12.67$

47.Sol. $R = \frac{K_2\,|P|}{K_1 + K_2}\left[1 - e^{-(K_1+K_2)t}\right]$

$$R = \frac{15\times10^{-2}\times4}{5\times10^{-2}+15\times10^{-2}}\left[1 - e^{-(5\times10^{-2}+15\times10^{-2})\times10}\right]$$

$$= \frac{60\times10^{-2}}{20\times10^{-2}}\left[1 - e^{-20\times10^{-2}\times10}\right]$$

$$= 3\left[1 - e^{-2}\right]$$

$$= 2.59$$

GATE 2020

48.Sol.: For enzyme catalysis:-

$$\text{Rate} = \frac{v_{max}[S]}{[S]+K_M}$$

$K_M \rightarrow$ Michale is mention constant

$$v_{max} = K_2[E_0]$$

$$\frac{1}{\text{Rate}} = \frac{K_m}{v_{max}[S]} + \frac{1}{v_{max}}$$

Slope: $\frac{K_M}{v_{max}} = 0.16\,s$

Intercept: $\frac{1}{v_{max}} = 2.12\ mol^{-1}L_5$

$$\Rightarrow \quad K_M = \frac{0.16\,s}{2.12\ mol^{-1}LS}$$

$$K_M = 0.075\ mol\ L^{-1}$$

49**Sol.:** $X \xrightarrow[k_1]{6\times10^{-2}} Y \xrightarrow[k_2]{9\times10^{-3}} Z$

$[X]_0 = 12.5$ moles

$t = 10$ min.

$$[Y]_{10} = [X_0]\left(\frac{k_1}{k_2 - k_1}\right)\left(e^{-k_1t} - e^{-k_2t}\right)$$

$$=\left[Y\right]_{10}=12.5\left(\frac{6\times10^{-2}}{9\times10^{-3}-6\times10^{-2}}\right)\left(e^{-6\times10^{-2}\times10}-e^{-9\times10^{-3}\times10}\right)$$

$$\Rightarrow \quad \left[Y\right]=5.4 \text{ moles}$$

50Sol.: Given, $A=4.3\times10^{15}\,s^{-1}$

$T = 25ºC = 298\ k$

As $$A=\frac{k_BT}{h}e^{-\Delta Hg}e^{\frac{\Delta S^{\#}}{R}}$$

$$4.3\times10^{15}s^{-1}=\frac{1.38\times10^{-23}\,Jk^{-1}\times298k}{6.626\times10^{-34}\,JS}\cdot e^{0}\cdot e^{\frac{\Delta S^{\#}}{8.314}}$$

$$\Rightarrow \quad 0.069\times10^{4}=e^{\frac{\Delta S^{\#}}{8.314}}$$

$$\Rightarrow \quad \ln\left(0.069\times10^{4}\right)=\frac{\Delta S^{\#}}{8.314}$$

$$\Rightarrow \quad \Delta S^{\#}=54.39$$

GATE 2021

51. Sol. According to Arrhenius theory

$$k=Ae^{-Ea/RT}$$

$$k_1=Ae^{-Ea/RT_1}$$

$$k_2=Ae^{-Ea/RT_2}$$

$$\frac{k_1}{k_2}=e^{-\frac{Ea}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

$$\ln\left(\frac{k_1}{k_2}\right)=-\frac{Ea}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\ln\left(\frac{0.237\times10^{-4}}{2.64\times10^{-4}}\right)=-\frac{Ea}{8.314}\left(\frac{1}{273}-\frac{1}{298}\right)$$

$$Ea=\frac{8.314\times273\times298}{25}\left[-\ln\left(\frac{0.237}{2.64}\right)\right]$$

$$Ea=65215.5 \text{ J/mol}$$

$$=65.2 \text{ kJ/mol}$$

QUANTA CHEMISTRY CLASSES
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6

SURFACE CHEMISTRY

GATE 2008

1. $\Gamma = \Gamma_0 e^{\varepsilon_a/kT} = 10^{-12}\ \text{sec}\ e^{\frac{16.628\times10^{3}\ \text{J/mol}}{8.31\times\frac{\text{J}}{\text{K}-\text{mol}}\times300\text{K}}} = 7.8\times10^{-10}$

Correct option is (a)

GATE 2011

2. According to conventional transition state theory for elementary bimolecular reactions the molar entropy of activation $\Delta S^{\#}$. is negative because two reactant specing come together to form one spacing.

Δng for Bimolecular Reactions is – 1

$\therefore\ \ \Delta S^0 < 0$

Correct option is (c)

GATE 2013

3. $\theta = \dfrac{kp}{1+kp} \Rightarrow \theta + \theta kp = kp \ \Rightarrow \theta = kp(1-\theta)\ \Rightarrow k = \dfrac{\theta}{1-\theta}\times\dfrac{1}{p} = \dfrac{0.01}{1-0.01}\times\dfrac{1}{10}$

Correct option is (0.001)

GATE 2014

4. $\theta = \dfrac{KP}{1+KP}$

For gas, P α concentration $\Rightarrow \quad \theta = \dfrac{K[X]}{1+K[X]}$

At very low concentration, $1 >> K[X] \Rightarrow \qquad \theta = K[X]$

Correct option is (a)

GATE 2015

5. $A_g(g) \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 2A\ ;\ \theta = \dfrac{(KP)^{1/2}}{1+(KP)^{1/2}}\ ;\ \dfrac{1}{\theta} = \dfrac{1+(KP)^{1/2}}{(KP)^{1/2}}\ ;\ \dfrac{1}{\theta} = \dfrac{1}{K_{eq}^{1/2}\sqrt{P}} + 1$

Slop is $\frac{1}{\sqrt{K_{eq}}}$

Correct option is (d)

GATE 2016

6. $$\frac{P}{V} = \frac{P}{V_m} + \frac{P}{KV_m}$$

$$\text{Slope} = \frac{1}{V_m} = 0.01 \Rightarrow V_m = 100$$

GATE 2017

7. $$\theta = \frac{(KP)^{1/2}}{1+(KP)^{1/2}} \qquad K = \frac{K_a}{K_d} = 4$$

$$\theta = \frac{(4\times1)^{1/2}}{1+(4\times1)^{1/2}} = \frac{2}{1+2} \Rightarrow \theta = \frac{2}{3} = 0.67$$

Correct answer is (0.67)

GATE 2018

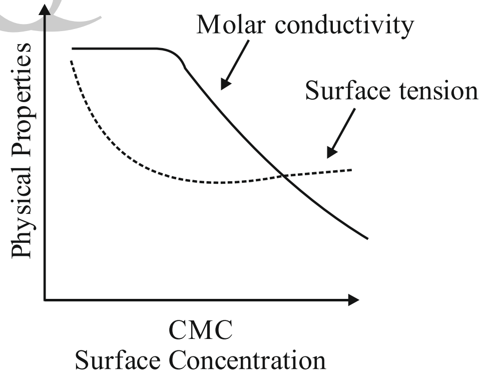
8. $$O_3 \longrightarrow \underset{0.33}{\underset{\downarrow}{O}} + \underset{0.33}{\underset{\downarrow}{O}} + \underset{0.33}{\underset{\downarrow}{O}} \quad \text{Triatomic; } \gamma = \frac{(kp)^{1/3}}{1+(kp)^{1/3}} \Rightarrow \frac{1}{3} = 0.33 \text{ (value of x)}$$

$$E_{wb} = h\nu = k_bT \qquad h\nu = k_BT,\ \nu = \frac{k_BT}{h}$$

The frequency os such vibration will below and average energy will be of the order of k_BT.

Correct option is (d)

9. Ionic micelle forming surfactant near its critical miscelle concentration (CMC)



Correct option is (b)

GATE 2019

10Sol. $Q = K(P)^{1/n} \rightarrow$ According to treundlich's isotherm

$$\ln Q = \ln K + \frac{1}{n}\ln P$$

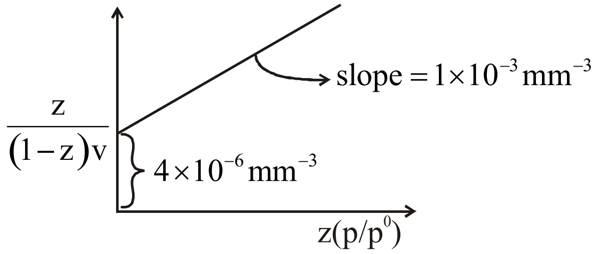
$$y = C + mx$$

Option B is correct.

11. SOL:

GATE 2020

12Sol.:



according to BET equation, we have

$$\frac{p}{(p^0 - p)v} = \frac{C-1}{v_m C}.\frac{p}{p^0} + \frac{1}{v_m C}$$

$$\Rightarrow \quad \frac{1}{v_m C} = 4\times10^{-6}\,mm^{-3}$$

$$\frac{C-1}{v_m C} = 1\times10^{-3}\,mm^{-3}$$

$$\Rightarrow \quad (C-1)4\times10^{-6} = 1\times10^{-3}$$

$$\Rightarrow \quad C - 1 = 0.25\times10^{3}$$

$$\Rightarrow \quad C = 251$$

$$\Rightarrow \quad \frac{1}{v_m \cdot 251} = 4\times10^{-6}\,mm^{-3}$$

$$\Rightarrow \quad v_m = \frac{1}{251\times4\times10^{-6}}$$

$$v_m = 996\,mm^3.$$

QUANTA CHEMISTRY CLASSES
An institute of Chemical Sciences

7

POLYMER

GATE 2016

1. $M_1 = 13.7$

$M_2 = 15.5$

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3}{N_1 + N_2 + N_3} = \frac{M_1 + M_2 + M_3}{3}$$

$M_3 = 17.2$

$N_1 = N_2 = N_2 = N$

$$\overline{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2}{N_1N_1 + N_2M_2 + N_3M_3} = \frac{M_1^2 + M_2^2 + M_3^2}{(M_1 + M_2 + M_3)}$$

$$\text{P.D.I.} = \frac{\overline{M}_w}{M_n}$$

Correct option is (a)

8

ELECTROCHEMISTRY AND CONDUCTANCE

GATE 2005

1. For reversible cell heat change is $T\Delta S^0$

   Correct option is (b)

2. $Cu \mid Cu^{2+}(aq) \parallel [Cu(NH_3)_4]^{2+}, aq\ NH_3 \mid Cu$

$$E^0 = \frac{0.0591}{n}\log K_{sc}$$

$$0.35 = \frac{0.0591}{n}\log K_{sc}$$

$$11.844 = \log K_{sc}$$

$$K_{sc} = 6.98 \times 10^{11}$$

   Correct option is (c)

3. According to Rault's law : Reltive lowering of vapour pressure is equal to he mole fraction of solute.

   Vapour pressure 298K of the solvent $(P^\circ) = 24$ torr

   Vapour pressure of the solution = (P)

   Now, relative lowering of vapour pressure = $\frac{P^\circ - P}{P^\circ}$

   Mole fraction of solue (NaCl) = $(x_{NaCl}) = 0.015$

$$\therefore \frac{P^\circ - P}{P^\circ} = x_{NaCl} \Rightarrow \frac{24 - P}{24} = 0.015$$

$$\Rightarrow 24 - P = 24 \times 0.015 \Rightarrow P = 24 - 0.36 = 23.64 \text{ torr}$$

   Correct option is (c)

4. Enthalpy of vapouruization = Δ_t/vapourization

$$\text{liquid} \rightleftharpoons \text{vapour}$$

$$\text{In}\ \frac{P_2}{P_1} = \frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\Rightarrow \ \text{In}\frac{760 \text{ torr}}{529 \text{ torr}} = \frac{\Delta H}{8.314 \text{ Jmol}^{-1}\text{K}}\left(\frac{373-363 \text{ K}}{373\times 363 \text{ K}_2}\right)$$

$$\Rightarrow \ \Delta H = \text{In } \frac{760}{529} = \frac{8.314\times 373\times 363}{10} \text{ Jmol}^{-1}$$

$\Rightarrow \ \Delta H = 40.787 \text{ Jmol}^{-1}$

$\Rightarrow \ \Delta H_{\text{vapourization}} = 40.787 \text{ kJ mol}^{-1}$

Correct option is (b)

GATE 2006

5. $Cu^{+}\,(aq) + e^{-} \rightarrow Cu(s)$ E0=0.52V

$Cu^{+}\,(aq) \rightarrow Cu^{2+}\,(aq) + e–$ $E_0 = 0.16$ V

Net reaction : $2\,Cu^{+} \rightarrow Cu(s) + Cu^{2+}\,(aq)$

$E^0_{cell} = E^0_{cath} - E^0_{anode} = 0.52 - 0.16 = 0.36$ V

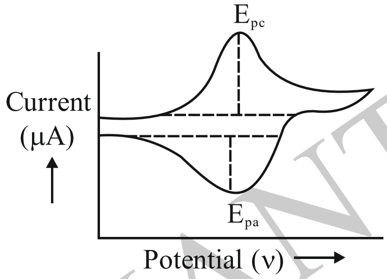
$\Delta G^0 = -\,nf\,E^0 = -1 \times 96500 \times 0.36 = -34740 \text{ J} = -34.7 \text{ kJ}$

Correct option is (a)

GATE 2007

6. $Cd^{2+} + 2e^{-} \rightleftharpoons Cd$

$(E_P)_{anodic}$ observed in cyclic voltametry at hanging mercury drop electrode is –650 mV vs SCE.



$$\Delta E_p = |E_{p,anodic} - E_{p,\,cathodic}| = \frac{59}{n}\text{mV}$$

$$\Rightarrow \ |-650 - E_{p\,,cathodic}| = \frac{59}{n}\text{mV} = 29.5 \text{ mV}$$

$\Rightarrow \ E_{p,\,cathodic} = -(650 + 29.5) \text{ mV} \simeq -679 \text{ mV}$

Correct option is (b)

7. $Fe^{3+} + 3e^{-} \rightarrow Fe$ $E_1 = -0.04$ V $\Delta G_1 = -n_1 f\,E_1$ ...(1)

$Fe^{2+} + 2e^{-} \rightarrow Fe$ $E_2 = -\,0.44$ V $\Delta G_2 = -n_2 f\,E_2$ ...(2)

From Eq. (1) & Eq. (2) gives required equation

$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$ $\Delta G = \Delta G_1 - \Delta G_2$

$-nf\,E = -n_1 f\,E_1 + n_2 f\,E_2$

$-f\,(nE) = -f(n_1\,E_1 - n_2 E_2)$

$$E = \frac{n_1E_1 - n_1E_2}{n}$$

$$E = -\frac{0.12 + 0.88}{1}$$

$$E = 0.76$$

Correct option is (a)

8. $MnCl_2 \rightarrow Mn^{2+} + 2Cl^-$

$n_{MnCl_2} = 25 \times 1.2 \times 10^{-3} = 30 \times 10^{-3} = 0.03$ mol

$\Rightarrow n_{Mn^{2+}} = 0.03$ mmol $\quad n_{Cl} = 2 \times 0.06 = 0.06$ mmol

$KCl \rightarrow K^+ + Cl^-$

$n_{KCl} = 35 \times 6 \times 10^{-4}$

$= 210 \times 10^{-4} = 0.021$ mmol

$\Rightarrow n_{K^+} = 0.021$ mmol $n_{Cl^-} = 0.021$ mmol

$\text{Total}_{n_{Cl^-}} = 0.06 + 0.021 = 0.081$ mmol $\quad V_{total} = 25 + 35 = 60$ mL

$$[Mn^{2+}] = \frac{0.03}{60} = 5 \times 10^{-4}\ M$$

$$[Cl^-] = \frac{0.081}{60} = 1.35 \times 10^{-3}\ M$$

$$[K^+] = \frac{0.021}{60} = 3.5 \times 10^{-4}$$

Correct option is (c)

9. Activity of Mn^{2+} ion in the above solution is

$a = a = \gamma_{mn^{2+}} \cdot C_{mn^{2+}} = 0.8 \times 5 \times 10^{-4} = 4 \times 10^{-4}$

Correct option is (d)

GATE 2008

10. $\log \gamma_\pm = -A|Z_+ Z_-| I^{1/2}$

$$I = \frac{1}{2}\left\{5\times10^{-4}\times4+2\times5\times10^{-4}\times1\right\}$$

$$= \frac{1}{2}\left\{20\times10^{-4}+10\times10^{-4}\right\}$$

$$I = 15 \times 10^{-4}$$

$$\log\gamma_\pm = -0.509\ |2 \times 1|\ (15 \times 10^{-4})^{1/2}$$

$$= -0.509 \times 2 \times 3.873 \times 10^{-2}$$

$$\log\gamma_\pm = -3.942 \times 10^{-2}$$

$$\gamma_\pm = 0.913$$

Correct option is (d)

GATE 2009

11. $KCl \longrightarrow K^+ + Cl^-$

$$In\gamma_\pm + -A|Z^+||Z^-| - A\left|Z^+\right|\left|Z^-\right|\sqrt{1};\ In\gamma_\pm \propto \sqrt{4} \Rightarrow In\ \gamma_\pm = -2A\left|Z^+\right|\left|Z^{-1}\right|\sqrt{I}$$

Decrease by factor 2

Correct option is (a)

GATE 2010

12. Metals with lower standard reduction potential can displace the metal with higher standard reduction potential from their solution. Mg with lower standard reduction potnetial (–2.34) can reduce both Zn^{+2} can reduce both Zn^{+2} (–0.76) and Fe^{+2} (–0.44).

Correct option is ()

GATE 2011

13. $NaCl \rightleftharpoons Na^+ + Cl^-$

1 molal 1 molal 1 molal

$$I = \frac{1}{2}m_1z_1^2 = \frac{1}{2}[1+1] = 1$$

$$\log\gamma_\pm = A\left|z + z -\right|\sqrt{I}; \qquad \log\gamma_\pm = -A\left|1 \times -1\right|\sqrt{I}$$

$$\log\gamma_\pm = -A \qquad [\gamma_\pm = 10^{-A}]$$

Correct option is (a)

14. $$M + \underset{(C_2)}{M^+\ (0.1)} \longrightarrow \underset{(C_1)}{M^+\ (0.01)} + M$$

$$E = \frac{-2.303RT}{nF}\log\frac{C_1}{C_2} \qquad \Rightarrow E = -\frac{2.303RT}{F}\log\frac{0.01}{0.10}$$

$$E = -\frac{2.303RT}{F}\log\frac{1}{10} \qquad \Rightarrow E = \frac{2.303RT}{F}$$

Correct option is (a)

GATE 2012

15. $Pt\ |H_2\ (1\ bar)|\ H^+\ (solution)\ ||\ Cl^-\ |Hg_2Cl_2|\ Hg$

$$E_{cell} = 0.7530\ V \qquad E^0_{Cl^-|Ag_2Cl_2|Hg} = 0.2802$$

At anode: $H_2 \longrightarrow 2H^+\ 2e^-$

At cathode: $Hg_2Cl_2 + 2e^- \longrightarrow 2\ Hg + 2Cl^-$

Net reaction: $H_2\ (g) + Hg_2\ Cl_2\ (s) \longrightarrow 2H^+_{(aq)} + 2Hg\ (s) + 2Cl^-\ (aq)$

$$E = E^0_{Cell} - \frac{0.0591}{2}\log[H^+]^2$$

$E = 0.2802 + 0.0591$ pH

$\boxed{pH = 8}$

Correct option is (c)

16. $2MnO_4^- + 5H_2C_2O_4 + 6H^+ \longrightarrow 2Mn^{+2} + 8H_2O + 10CO_2$

$E^0\ (MnO_4^-/Mn^{+2}) = 1.5$ IV

$E^0\ (CO_2/H_2C_2O_4) = -\ 0.9$

$MnO_4^- + 5e^- \longrightarrow Mn^{+2} \times 2$

$2CO_2 + 2e^- \longrightarrow C2O_4^{-2}$

$2MnO_4^- + 5C_2O_4^{-2}\ 6H^+ \longrightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$

Total number of electron = 10

$\Delta G = -RT\ In\ K$

$-nFE = -\ RT2.303\log K$

$$\log k = \frac{nFE}{2.303RT};\ E = E^0_{right} - E^0_{left} = 1 - 51 - (-0.49) = 2V;\ \log k_C = \frac{10\times 2}{0.0591} = 338$$

$\boxed{k_C = 10^{338}}$

Correct option is (b)

GATE 2013

17. $M_2X \rightleftharpoons 2M^- + X{-}2$

2S S (Solubility)

$k_{sp} = (2s)^2\ (s) = 4s^3$

When actually in the form of ion is ksp

$M2X \rightleftharpoons 2M^- + X{-}2$

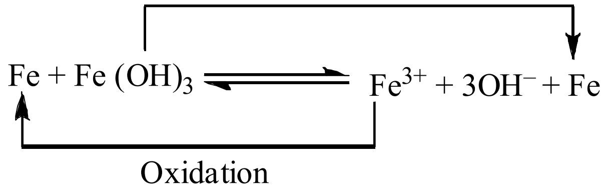
$(2a_+)$ (a_-)

$\left(2\gamma_+(m_+)^2\right)$ $(\gamma_- m_-)$

Correct option is (d)

18. $Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$

Metal insoluble due to K_{sp} reduction



$$= \quad E^0_{cell} = E^{0\,cathode}_{reduction} - F^{0\quad anode}_{red} = E^0_{OH^-|Fe(OH)_3|Fe} - E^0_{Fe^{3+}|Fe} = -0.786 + 0.036$$

$$= \quad 0.786 - 0.036 = -\,0.750 \text{ volt}$$

Correct option is (b)

19. $$E^0_{cell} = \frac{0.0591}{n}\log_{10} K_{sp} \Rightarrow \frac{-0.75\times 3}{0.0591} = \log_{10} K_{sp} \Rightarrow -38.2 = \log_{10} K_{sp}$$

In $K_{sp} = 2.303 \times \log_{10} K_{sp} = 2.303 \times (-38.2) = -87.97$

Correct option is (d)

GATE 2014

20. $Fe^{3+} + e^- \rightarrow Fe2+ = E^0 = 0.77$ V

$$E = E^0 - \frac{0.0591}{n}\log\frac{[Fe^{2+}]}{[Fe^{3+}]};\; E = E^0 - \frac{0.0591}{n}\log\left(\frac{0.1}{0.1}\right) \Rightarrow E = E^0 = 0.77 \text{ V}$$

$$\text{Now, } \underset{(1M)}{Fe^{3+}} + e^- \rightarrow \underset{(0.1M)}{Fe^{2+}};\; E = E^0 - \frac{0.0591}{1}\log\left(\frac{0.1}{1}\right) = 0.77 + 0.0591$$

$E = 0.8291V$

Correct option is (0.8291).

GATE 2015

21. $$Mn^{6+} \xrightarrow{1.28V} Mn^{4+} \xrightarrow{0.96V} Mn^{3+} \xrightarrow{1.5V} Mn^{2+}$$

$Mn^{5+} + e^- \longrightarrow Mn^{5+} \quad E^0_1 = 1.28$ V

$Mn^{5+} + e^- \longrightarrow Mn^{4+} \quad E^0_2 = 2.9$ V

$Mn^{4+} + e^- \longrightarrow Mn^{3+} \quad E^0_4 = 0.96$ V

$Mn^{3+} + e^- \longrightarrow Mn^{2+} \quad E^0_4 = 1.5$ V

$$Mn^{6+} + 4e^- \longrightarrow Mn^{2+} \quad E^0 = \frac{n_1E^0_1 + n_2E^0_2 + n_3E^0_3 + n_4E^0_4}{n}$$

$$= \frac{1.28 + 2.9 + 0.96 + 1.5}{4} = 1.66$$

22. $$E + S \underset{K_2}{\overset{K_1}{\rightleftharpoons}} ES \underset{K_4}{\overset{K_3}{\rightleftharpoons}} P + E$$

$$E + S \underset{K_2}{\overset{K_1}{\rightleftharpoons}} ES \quad K' = \frac{K_1}{K_2}$$

$$ES \underset{K_2}{\overset{K_1}{\rightleftharpoons}} P + E \quad K'' = \frac{K_3}{K_4}$$

Net process $E + S \rightleftharpoons P + E \quad K = K' . K'' \qquad K = \frac{K_1}{K_2} \cdot \frac{K_3}{K_4}$

Correct option is (a)

23. $E^0_{cell} = \frac{0.0591}{n} \log K_{sp}; E^0_{Ag|ArBr|Br^-} - E^0_{Ag^+|Ag} = \frac{0.0591}{n} \log K_{sp}$

$0.07 - E^0_{Ag^+|Ag} = 0.0591 \log (5 \times 10^{-13}); 0.07 - E^0_{Ag^+|Ag} = -0.726; \; E^0_{Ag^+|Ag} = 0.796$ V

Correct option is (0.79 to 0.82)

24. $\log \gamma_{\pm} = -A |Z_+ Z_-| I^{1/2}$

$I = \frac{1}{2} \{0.001 \times 2^2 + 0 \times 0.001 \times 2^2\} = \frac{1}{2} \{0.004 + 0.004\} \Rightarrow I = 0.04$

$\log \gamma_{\pm} = -0.1287 \Rightarrow \gamma_{\pm} = 0.743$

Correct option is (0.73 to 0.75)

25. $i_d = 607 \, nD^{1/2} \, cm^{2/3} \, t^{1/6}$

$i_d = 607 \times 2 \times (1.2 \times 10^{-5})^{1/2} \times 3 \times 10^{-4} \times 3^{2/3} \times 3^{1/6}$

$i_d = 1214 \times 3.46 \times 10^{-3} \times 3 \times 10^{-4} \times .20649 \times 1.2$

$i_d = 31248.93 \times 10^{-7} \, \mu_{amp}$ or $i_d = 0.00312 \, \mu A$

Correct answer is (0.00312)

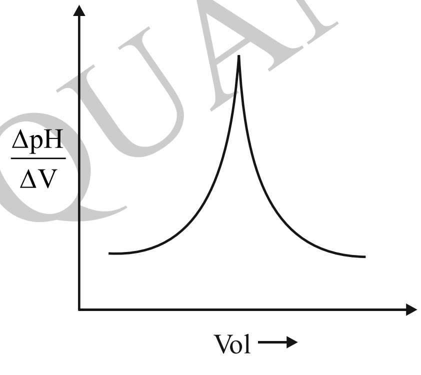
GATE 2016

26. For strong acid vs strong base $E = E^0 + 0.0591$ pH.

Plot of E vs volme of base will have semi shape as pH as volume

Similarly, for other plots too.

Since,



is correct

Correct option is (c)

GATE 2017

27. $D = \frac{\mu k_B T}{q} = \frac{6 \times 10^{-8} \times 1.38 \times 10^{-23} \times 300}{1.6 \times 10^{-19}} = \frac{2484 \times 10^{-31}}{1.6 \times 10^{-19}} = 1552 \times 10^{-12} = 1.552 \times 10^{-9} \, m^2 s^{-1}$

$\Rightarrow$ X is 1.552

Correct answer is (1.55)

28. $\gamma_{Ca^{2+}} = 0.72 = \gamma_+ \qquad Caf_2 \to Ca^{2+} + 2f^-$

$\gamma_{f^-} = 0.28 = \gamma_- \qquad x = 1\ y = 2$

$(\gamma_\pm)^{x+y} = y_+^x.\gamma_-^y \Rightarrow (\gamma_\pm)^3 = (0.72)^1\,(0.28)^2$

$(\gamma_\pm)^3 = 0.056448 \Rightarrow \gamma_\pm = 0.387 \approx 0.39$

Correct answer is (0.39)

29. $I_d = 300\ \mu A$ at concnetration 'C'

$C' = C + 0.1\ \ I_d^{'} = 900\ \mu A$

$I_d \propto C$

$$\frac{I_d}{I_d^{'}} = \frac{I_d}{I_d^{'}} = \frac{C}{C+0.1} \Rightarrow \frac{300}{900} = \frac{C}{C+0.1} \Rightarrow \frac{1}{3} = \frac{C}{C+0.1} \Rightarrow 3 = 1 + \frac{0.1}{C} \Rightarrow \frac{0.1}{C} = 2 \Rightarrow C = \frac{0.1}{2} = 0.05$$

Correct answer is (0.05)

GATE 2018

30. $\Delta S = nF\left(\frac{\partial F}{\partial T}\right)_P \Rightarrow \left(\frac{\partial F}{\partial T}\right)_P = \frac{\Delta S}{nF}$

Correct option is ( )

31. $O_2 + 2H^+ + 2e^- \to H_2O_2 \quad E_1 = +0.70V \qquad \Delta G_1 = -n_1FE_1 \qquad ...(1)$

$H_2O_2 + 2H^+ + 2e^- \to 2H_2O \qquad E_2 = +1.76V \qquad \Delta G_2 = -n_2FE_2 \quad ...(2)$

$O_2 + 4H^+ + 4e^- \to 2H_2O \quad E = ? \qquad ...(3)$

On adding (1) and (2), we obtain equation (3)

32. $C = 0.01\ M \qquad \Lambda_m = 64.4\ Scm\ mol^{-1}$

$\frac{\ell}{A} = 0.4\ cm^{-1} \qquad \Lambda_{H^+}^{\infty} = 350;\ \Lambda_{X^+}^{\infty} = 410\ Scm^2\ mol^{-1}$

$\Lambda_m^{\infty}(HX) = 350 + 410 = 760\ Scm\ mol^{-1}$

$$K_a = \frac{C\Lambda_m^2}{\Lambda_m^{\infty}\left(\Lambda_m^{\infty} - \Lambda_m\right)}$$

$$\Rightarrow\ k_a = \frac{0.01 \times 64.4 \times 64.4}{760 \times 695.6} = 7.845 \times 10^{-5}$$

$pk_a = -\log k_a = -\log(7.845 \times 10^{-5}) = 5 - \log 7.845$

$\boxed{pk_a = 4.105}$

$\Rightarrow\ \Delta G = \Delta G_1 + \Delta G_2$

$-nFE = -n_1FE_1 - n_2FE_2$

$$nE = n_1E_1 + n_2E_2$$

$$E = \frac{(2\times 0.7) + 2\times(1.76)}{4} = \frac{1.4+3.52}{4} = 1.23\ \text{V}$$

Correct answer is (1.23)

GATE 2019

33.Sol. $M(s) \mid MI_2(s) \mid MI_2(aq) \mid M(s)$

Anode: $M + 2I^- \rightarrow MI_2 + 2e^-$

Cathode: $M^{2+} + 2e^- \rightarrow M$

$M^{2+} + 2I^- \rightarrow MI_2$

$$E^o_{cell} = E^0_{M|MI_2|I^+} + E^0_{M^{2+}|M}$$

$$= 0.36 - 0.12$$

$$= 0.24\ \text{V}$$

Using

$$\Delta H^o = -nF(E^o - T.T)$$

$$= -(2)(96500)\,[E^o - 298\,(1.5\times 10^{-4})]$$

$$= -(2\times 96500)\,(0.24 - 298\times 1.5\times 10^{-4})$$

$$= -37.693\ \text{kJ mol}^{-1}$$

GATE 2020

34Sol.: $CuSO_4 \rightarrow \underset{m}{Cu^{2+}} + \underset{m}{SO_4^{2-}}$

$$\text{activity} = (m.\gamma_\pm)(m.\gamma_\pm)$$

$$\text{activity} = m^2\gamma_\pm^2$$

35Sol.: $Ag \mid AgBr(s) \mid Br^-(a=0.20),\ Cu^{2+}(a=0.48),\ Cu^+(a=0.24) \mid Pt$

Anode: $Ag(s) + Br^-(aq) \longrightarrow AgBr(s) + e^-$

Cathode: $Cu^{2+} + e^- \longrightarrow Cu^+$

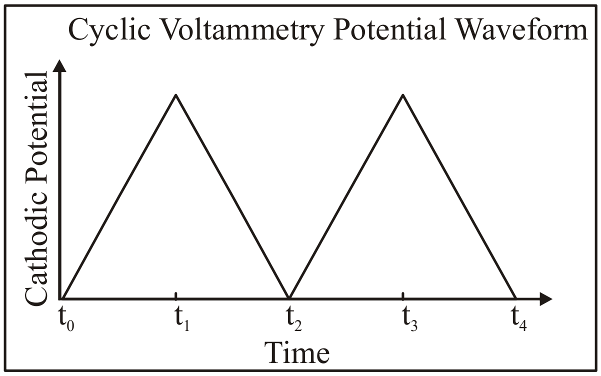
$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\log\frac{[Cu^+]}{[Cu^{2+}][Br^-]}$$

$$0.082 - \frac{0.0591}{1}\log\frac{(0.24)}{(0.48)(0.20)}$$

$$\Rightarrow \quad E_{cell} = 0.058\ \text{V}$$

QUANTA CHEMISTRY
CLASSES

36Sol.:



GATE 2021

37Sol. Applying Faraday law

$w = Z\,I\,t$

mass of Ag^+ deposited as Ag $(Ag^+ + e^- \rightarrow Ag)$

$$W = \frac{107.9}{1 \times F} \times 0.7 \times 10 \times 60$$

$= 0.469$ g

Similarly for Cu^{2+} dissolve using and are charge

$W = Z \times 1t$

$$W = \frac{63.5}{z \times 96485} \times 0.7 \times 10 \times 60 \qquad Cu \rightarrow Cu^{2+} + 2e^-$$

$= 0.138$ g

Correct option is (c)

38Sol. Charge = I × t

$= 1.5 \times 2 \times 60 \times 60$ sec

$= 3 \times 60 \times 60$

$= 10800$

QUANTA CHEMISTRY CLASSES
An institute of Chemical Sciences

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SOLID STATE

GATE 2005

1. Conduction band is empty in solid sodium chloride
Correct option is (b)

GATE 2006

2. $\rho = \frac{ZM}{Na^3}$

$$a = \left(\frac{ZM}{N\rho}\right)^{1/3} = \left(\frac{(2\times 137.3)}{6.023\times10^{23}\times3.62\text{cm}^{-3}}\right)^{1/3} = 5.01 \times 10^{-8}$$

$$r = \frac{a\sqrt{3}}{4} = \frac{5.01\times10^{-8}\times1.7325}{4} = 2.2 \times 10^{-8}$$

Correct option is (d)

3. The arrangement of sulphur in zinc blende and wurtzite structures, are cubic close packing and hexagonal close packing respectively
(Correct option is (b)

GATE 2008

4. Lattice parameters for monoclinic $a \neq b \neq c \Rightarrow \alpha = \beta = 90° \neq \gamma$
Correct option is (*)

5. As a result of this defect some of the Ni^{2+} ions oxidise into NI^{3+} ions and decrease the dficiency of electrons and semiconductor will be p-type.
Correct option is (c)

6 Sol: ?

7. $\lambda = \frac{h}{\sqrt{2meV_{min}}} \Rightarrow 2d = \frac{h}{\sqrt{2me\ V_{min}}}$

$$\Rightarrow\ 2meV_{min} = \frac{h^2}{4d^2} \Rightarrow V_{min} = \frac{h^2}{4d^2\times2me}$$

$$= \frac{6.63\times10^{-34}\times6.6\times10^{-34}}{4\times351.8\times351.8\times10^{-24}\text{m}\times2\times9.1\times10^{-34}\times1.6\times10^{-19}}$$

$$= \frac{6.63\times6.63\times10^{6}}{14415942} = 3$$

Correct option is (d)

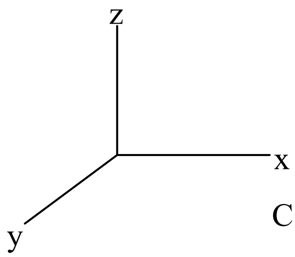
GATE 2009

8. $2d \sin\theta = n\lambda$; $3 \times d \times \sin 1587 = 1 \times 1.54 \times 10^{-8}$ cm

$$d = \frac{1.54\times10^{-8}\text{cm}}{2\times51n15.87}; d = \frac{1.54\times10^{-8}\text{cm}}{2\times0.27}$$

$$d = \frac{1154\times10^{-8}\text{cm}}{154} = 2.85 \times 10^{-8}\text{ cm} = 2.85 \times 10^{-8} \times 10^{-2}\text{ mtr} = 2.85 \times 10^{-10}\text{ mtr} = 2.85 \times \text{Å} = 2.85$$

Correct option is (b)

9. 

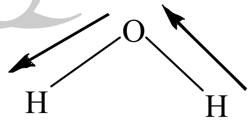
Basic set = 3

Cartesian coordinate

C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}
x	1	−1	1	−1
y	1	−1	−1	1
z	1	1	1	1

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
R.R.	3	−1	1	1

Correct option is (d)

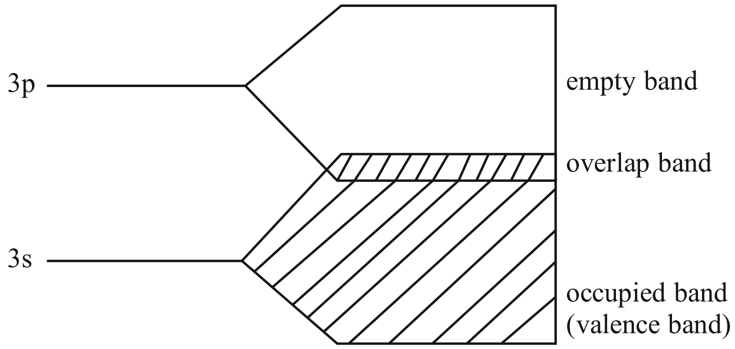
10. 

In asymmtric stretching C_2 is absent only molecular plane is present. So, irreducible representation corresponding to B_1.

Correct option is (b)

GATE 2010

11. The electric configuration of Mg–$3s^2 3p°$(Ne). The energy gap between 3s and 3p is small hence they the 3s orbital and can overlap with 3p orbital band. So, pertubation from



filled valence band to empty conduction band can take place, making magnesium conductor.

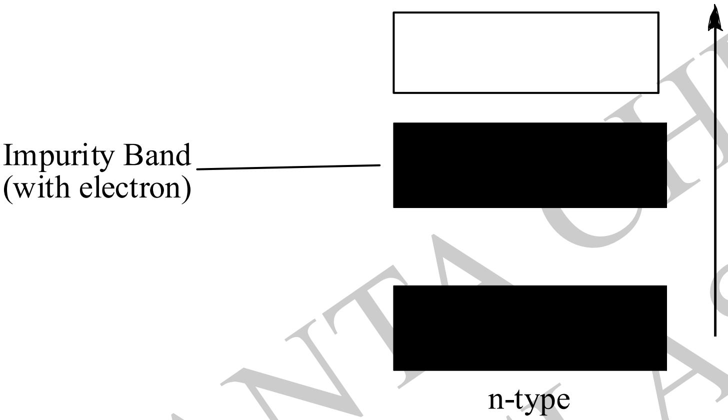
Correct option is (c)

GATE 2011

12. In semiconductors there appears an impurity band between valence band and cnductivity band.

In n-type of semiconductor the impurity band contain electrons while in p-type conductors impurity band is empty.

But in both case the impurity band show bridge between valence band and conduction band.



Correct option is (a)

GATE 2012

13. For FCC h, k, l should be all either even or all odd.

$2d \sin\theta - n\lambda = 1\lambda$ {considering first order of reflection}

$$2\frac{a}{\sqrt{h^2+k^2+\ell^2}}\sin\theta = \lambda \Rightarrow \sin\theta = \frac{\lambda}{2a}\sqrt{h^2+k^2+\ell}$$

θ will be minium for (1 1 1)

Correct option is (b)

GATE 2013

14. A crystal has the lattice parameters $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$. The crystal system is orthorhombic.

Correct option is (d)

15. $d = \frac{a}{\sqrt{2}} - \frac{4.20}{1.414} = 2.97$

Correct option is (b)

GATE 2014

16. $\rho = \frac{ZM}{Na^3}; \rho = \frac{2\times96}{6.023\times10^{23}\times0.314\times0.314\times0.314\times10^{-27}\,mtr^3} = \frac{2\times96\times10^4}{0.1864} = 10137$

Correct option is (10137).

GATE 2015

17. Frenkel defect is an anion vacancy and a cation interstitial

Correct option is (b)

18. $d = \frac{a}{\sqrt{h^2+k^2+\ell^2}} \Rightarrow d = \frac{a}{\sqrt{1^2+1^2+0}} \Rightarrow d = \frac{a}{\sqrt{2}}$

Correct option is (d)

GATE 2016

19. When crystas of sodium chloride are hated in the presence of sodium vapour they turn yellow due to the formation of F-centres.

Correct option is (c)

20. p-type semiconductor formed by doping Si with B

Correct option is (d)

GATE 2017

21. In Mg valence 3s is fulled and it overlaps with empty 3p concution hand

Correct option is (d)

22. For NaCl, numbe of formula units for unit cell

$Z = 4 \Rightarrow FCS \Rightarrow F$

$CsCl, Z = 1 \Rightarrow SCC \Rightarrow P$

Na = Body centre + Edge centre

$Z\text{-}Na^+ = 1 \times 1 + 12 \times (1/4) = 1 + 3 = 4$

Cl^- = Corner centre + face centre

$Z\text{-}Cl^- = 8 \times (1/8) + 6 / (1/2) = 1 + 3 = 4$

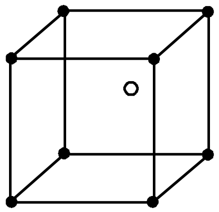
Cs = body cente = $1 \times 1 = 1$

Cl = corner = $8 \times (1/8) = 1$

Correct option is (b)

GATE 2019

23Sol. Ans. (b)



● $Cl^{-} \rightarrow SCC \rightarrow$ i.e. Cl^{-} at 8 corner

○ $Cs^{+} \rightarrow$ at cubical void

Generally, people consider it as BCC/since they assume that atoms/ion are at 8 corner and at Body center. But this is not true.

CsCl has SCC or premitive lattice with Cs^{+} at cubical void.

This is proved by structure factor concept.

GATE 2020

24Sol.: $n\lambda = 2d\sin\theta$

$$d = \frac{\lambda}{2\sin\theta} = \frac{1\cdot 54Å}{2\sin 16.8}$$

$d = 2.66$ Å

For cubic crystal system,

$$d_{hk\ell} = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}}$$

$$a = 2.66\sqrt{1+1+1}$$

$a = 4.61$ Å

25Sol.: Density of AgX = 6477 kg/m^3

$a = 577.5$ pm

AgX crystallizes in rock salt str.

So, $Z = 4$

as $\rho = \frac{Z \times M}{a^3 \times Na}$

$$\Rightarrow \quad 6477 = \frac{4 \times M}{(577.5)^3 \times \left(10^{-12}\right)^3 \times 6.022 \times 10^{23}}$$

$$\Rightarrow \quad \frac{10^{-3} \times 6477 \times 1.15 \times 10^{9} \times 10^{-13}}{4} = M$$

$= 186.2$ g/mol $=$ M(AgX)

As atomic weight of Ag is 107.87 g/mol

So, atomic weight of X is $\rightarrow 186.2 - 107.87 = 78.33$ g / mol

10

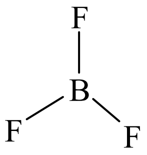
GROUP THEORY

GATE 2006

1. C_2 (axis) $\perp$ reflection $\sigma = S2$
Correct option is (b)

2. In C_{3v} point group character table
$A_1 \rightarrow A_2$ $A_1 = 1\ 1\ 1;\ A_2 = 1\ 1\ -1$
$A_1 \times A_2 = 1\ \ 1$ -1 [Rz] → not allowed
Correct option is (d)

3.



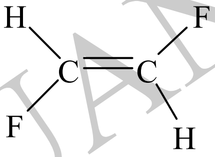
1 C_3
$3C_2$ (axis)
$3\sigma_v$ (plane)
$1\sigma_h$ (plane)

Correct option is (a)

GATE 2007

4. S_2 operation on a molecule with axis of rotation as the z-axis inversion occur
(–x –y –z)
Correct option is (d)

5.

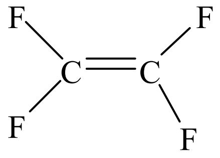


Trans 1-2 difluroethylene

Molecule having C_{2h} point group. Distionct symmetry operation E C_2 σ_h
Correct option is (b)

6. Number of irreducible representation is 4,
A_g, B_b, A_u, B_u
Correct option is (d)

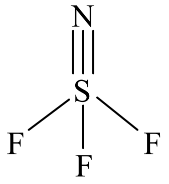
7.



Correct option is (d)

GATE 2008

8. Point group of NSF_3



One C3, $3\sigma_v$, C_{3v} point group

9. For the Td point group,

Td	E	$8C_3$	$3C_2$	σS_4	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
E	2	−1	2	0	0
T_1	3	0	−1	1	−1
T_2	3	0	−1	−1	1

Two three dimensional irreducible respectively

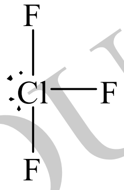
Two one diemensional irreducible respectively

One two dimensional irreducible respectively

Correct option is (b)

GATE 2010

10.



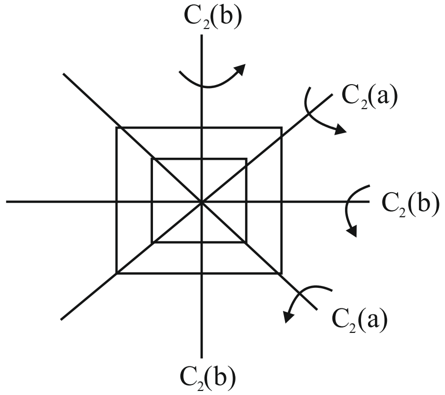
[One C2, $2\sigma_v$ hence, C_{2v} point group]

For C_{2v} point group, four irreducible representation

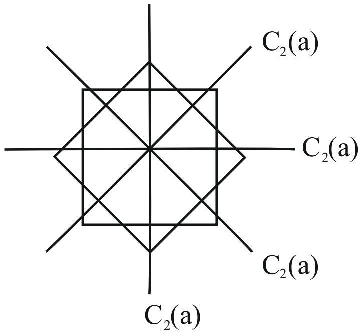
Correct option is (b)

GATE 2012

11.



Eclipsed form



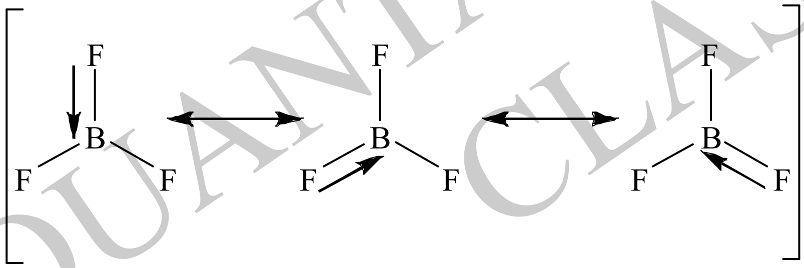
Staggered form

Symmetry operator of the four C_2 axis perpendicular to the principal axis belong to the same class in D_{4d}
Correct option is (b)

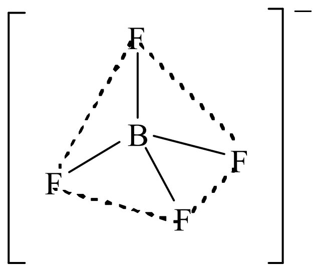
GATE 2013

12. $CH_2 = C = CH_2$
$C_2 + 2C_2 + 2\sigma_v + 1\sigma_d \rightarrow$ point group (D_{2d} point group)
Correct option is (d)

13. In BF_3, 'B' is sp^3 hybridised and there is B–F 'π' back donation, due to which B–F bond order increases and hence bond length decreased. B–F bond length is 130 pm.
Also BF_3 is trigonal planar.



In BF_4^- (tetra fluoro borate) 'B is sp^3 hybridised and there is no back donation. Hence B–F bond order is one.
$[BF_4]^-$ perfect Td.

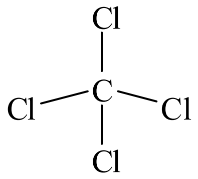


The B–F bond length is 145 pm.

Correct option is (a)

GATE 2014

14. Number of C_2 axis in CCl_4 is 3



Td – $3C_2$ axis

GATE 2020

15Sol.:

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$
Γ	12	0	2		

$$\eta_{A_1} = \frac{1}{6}\left[1.1.12 + 2.1.0 + 3.1.2\right] = 3$$

$$\eta_{A_2} = \frac{1}{6}\left[1.1.12 + 2.1.0 + 3(-1)(2)\right] = 1$$

$$\eta_{E} = \frac{1}{6}\left[1.2.12 + 2.(-1).0 + 3(0)(2)\right] = 4$$

Total modes = $3A_1 + A_2 + 4E$
Translational = $-A_1 \quad -E$
Rotational = $\underline{\qquad -A_2 \;\; -E}$
Vibrational = $2A_1 + 2E$
So, Raman active modes are $2A_1 + 2E$.

GATE 2021

16. Sol : ?

11

PHYSICAL SPACTRA

GATE 2005

1. Resonant frequencies for EPR and NMR are radio frequency and microwave region.

Correct option is (c)

2. rotational transition $\Delta J = \pm 1$

vibrational transition $D\nu = \pm 1$

NMR spectroscopy $\Delta m_I = \pm 1$

Electronic transition $\Delta \ell = \pm 1$

Correct option is (c)

3. Mercury arc is not excitation source for IR spectrometer.

Correct option is (d)

GATE 2006

4. Zero point energy $= \frac{1}{2}h\nu$

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \Rightarrow \mu = \frac{m_1 m_2}{m_1 + m_2} = \left(\frac{35\times35}{35+35}\right)1.67\times10^{-27}\,\text{kg} = \frac{35\times35}{70}\times1.6\times10^{-27}\,\text{kg}$$

$$\frac{1}{2}\times6.63\times10^{-34}\ \text{J}-\text{sec}\times\frac{1}{2\times3.14}\sqrt{\frac{2293.8\ \text{Nm}^{-1}}{\frac{35\times35}{70}\times1.67\times10^{-27}\ \text{kg}}} = 14.4\times10^{-21}\ \text{J-sec}$$

Correct option is (b)

5. $CO_2 \rightarrow$ microwave inactive

$SF_6 \rightarrow$ rotational microwave inactive

$H_2 \rightarrow$ rotational infrared inactive

$HCl \rightarrow$ rotational microwave active

Infrared active, rotational Raman active

Correct option is (c)

GATE 2007

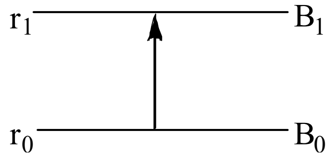
6. For p branch in the rotational vibrational spectra

$\Delta J = -1,\ \Delta v = +1$

Correct option is (c)

GATE 2008

7.



% change in internuclear distance is $\left(\frac{r_1 - r_0}{r_0} \times 100\right)$

$$B_1 = \frac{h}{8\pi^2 I_1 C} \qquad \frac{B_1}{B_0} = \frac{I_0}{I}$$

$$B_0 = \frac{B_1}{B_0} = \frac{r_0^2}{r_1^2}$$

$$\frac{r_0}{r_1} = \sqrt{\frac{B_1}{B_0}} \Rightarrow \frac{r_0}{r_1} = \sqrt{\frac{1.6\ \text{cm}^{-1}}{1.9\ \text{cm}^{-1}}} \Rightarrow \frac{r_0}{r_1} = 0.917$$

$$\% = \left(\frac{r_1 - r_0}{r_0} \times 100\right) = \left(\frac{r_1}{r_0} - 1\right) \times 100 = (1.009 - 1) \times 100 = 0.089 \times 100 = 8.9 \simeq 9\%$$

Correct option is (a)

8. $\overline{\omega}_e [1 - 2\,Xe] \rightarrow 2144\ \text{cm}^{-1}$ ...(1)

$2\,\overline{\omega}_e [1 - 3\,Xe] \rightarrow 4262\ \text{cm}^{-1}$ ...(2)

$\overline{\omega}_e - 2\,\overline{\omega}_e Xe = 2144\ \text{cm}^{-1}$ ...(3)

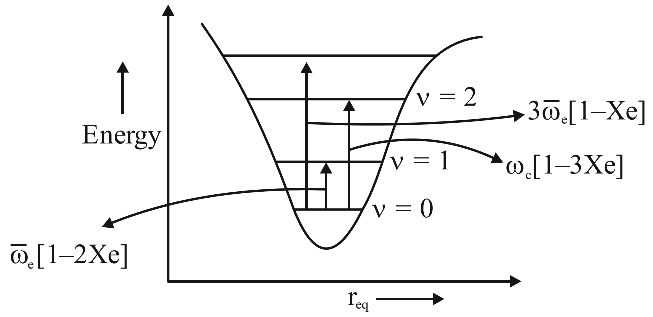
$2\,\overline{\omega}_e - 6\,\overline{\omega}_e Xe = 4262\ \text{cm}^{-1}$...(4)

Equation (1) multiply (3) and substract from (2)

$3\,\overline{\omega}_e - 6\,\overline{\omega}_e\ Xe = 6432$ cm–1

$$\frac{2\overline{\omega}_e - 6\overline{\omega}_e Xe = 4262\ \text{cm}^{-1}}{\overline{\omega}_e \qquad = 2170\ \text{cm}^{-1}}$$

$\overline{\omega}_e = 2170\ \text{cm}^{-1}$



Fundamental transition at 2170 cm^{-1}

Correct option is (b)

9. Anharmonicity constant,

$\omega\overline{e}\,[1-2\,Xe] = 2144\ cm^{-1}$

$\Rightarrow\ 2170[1-2\,Xe] = 2144\ cm^{-1}$

$$[1-2\,Xe] = \frac{2144}{2170} = 0.988$$

$\Rightarrow\ 1-2\,Xe = 0.988$

$\Rightarrow\ -2Xe = 0.988-1$

$$\Rightarrow\ -2Xe = -0.012 \quad \Rightarrow\ Xe = \frac{0.012}{2} = 0.006$$

Correct option is (c)

GATE 2009

10. For H_2, $\overline{v} = 4403.2\ cm^{-1}$; For I_2, $\overline{v} = 214.5\ cm^{-1}$, T = 300 K

We know that, $\frac{n_2}{n_1} = \frac{g_2}{g_1}\,e^{-\Delta\varepsilon/kT}$

$$\frac{n_2}{n_1} = \frac{1}{1}e^{\frac{-hc\overline{v}}{kT}} \Rightarrow \frac{n_2}{n_1} = e^{-\frac{hc\overline{v}}{kT}} \quad ...(1)$$

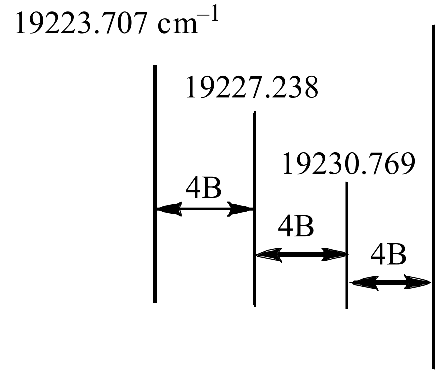
$$\text{For } H_2,\ \frac{n_2}{n_1}\,e^{-\frac{6.26\times10^{-34}\,J\,sec\times3\times10^{10}\,cm/sec\times4403.2\,cm^{-1}}{1.38\times10^{-23}\,J/K\times300K}}$$

$$= e^{-211.41}\times e^{-211.41\times10^{-1}} = e^{-21.14} = 6.75\times10^{-10} \simeq 7\times10^{-10}$$

$$\text{For } I_2,\ e^{-\frac{6.626\times10^{-34}\times3\times10^{10}\times214.5}{1.38\times10^{-23}\times300}} = e^{-10.29\times10^{-1}} = e^{-1.29} = 0.298 \simeq 3\times10^{-1}$$

Correct option is (b)

11.



4B = 19230.769 – 19227.238

4B = 3.531

B = 88275 cm^{-1}

B = 0.88275 cm^{-1} × c = 0.88275 × cm^{-1} × 3 × 10^{10} cm/sec

B = 26.484 × 10^9 Hz = 26.484 GHz

GATE 2010

12. $$J_{max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} = \sqrt{\frac{1.38\times10^{-23}\times300}{2\times6.6\times10^{-34}\times3\times10^{10}\times8.5}} - \frac{1}{2}$$

$$= \sqrt{\frac{1.38\times3000}{2\times6.6\times3\times8.5}} - \frac{1}{2} = \sqrt{\frac{4140.00}{39.6\times8.5}} - \frac{1}{2} = = \sqrt{\frac{4140}{39.6\times8.5}} - \frac{1}{2} = \sqrt{\frac{4140}{336.6}} - \frac{1}{2}$$

$$\sqrt{12.29} - \frac{1}{2} = 3.5 - 0.5 = 3$$

Correct option is (b)

13. $$\Delta v_1 \propto \frac{1}{\tau_1} \Rightarrow \frac{\Delta v_1}{\Delta v_2} = \frac{T_2}{T_1} \Rightarrow \frac{1.0}{0.2} = \frac{T_2}{T_1} \Rightarrow \frac{5}{1} = \frac{T_2}{T_1} \qquad \Delta v_1 : \Delta v_2 = 5 : 1 \text{ width ratio}$$

$T_1 : T_2 = 1.5$

Lifetime ratio

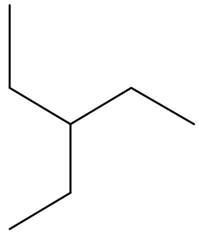
Correct option is (b)

GATE 2011

14. The region of electromagnetic spectrum employed in the electron spin resonance (ESR) is microwave [3 × 10^{10} – 3 × 10^{12} Hz]

Correct option is (b)

15.



One C_3 axis, oine σ_h, C_{3h} point group

Correct option is (c)

16. $\Delta E = v = 0$ to $v = 1$

$\Delta E = h\nu$ (for SHO)

$h\nu$ in joule

$$\frac{h\nu}{hc} = \frac{v}{c}\,cm^{-1} \qquad \Rightarrow \bar{v} = \frac{v}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

Wave number

$$= \frac{1}{2\pi \times 3 \times 10^{10}}\,cm/sec\sqrt{\frac{8 \times 10^2\,N.m^{-1}}{2 \times 10^{-26}\,kg}} = \frac{1}{2\pi \times 3 \times 10^{10}\,cm/sec}\sqrt{\frac{8 \times 10^2\,kg\ mtr\ mtr^{-1}}{2 \times 10^{-26}\,sec^2 + kg}}$$

$$= \frac{1}{2 \times 3.14 \times 3 \times 10^{10}\,cm/sec}\frac{1}{sec}\sqrt{\frac{8 \times 10^2}{2 \times 10^{-26}}}$$

$$= \frac{2 \times 10^{14}}{6 \times 3.14 \times 10^{10}} = \frac{10000}{9.14} = 106.14$$

Correct option is (c)

17. $J = 0$ to $J = 1$

$$2B = B = \frac{h}{8\pi^2 Ic}$$

$$= \frac{2 \times h}{8\pi^2 Ic} = \frac{2 \times 6.6 \times 10^{-34}\ J.s}{8 \times 3.14 \times 3.14 \times 2 \times 10^{-26} \times 3 \times 10^{10}\,cm/s \times 100 \times 10^{-12}\,mtr \times 100 \times (-1.2)mtr}$$

$$= \frac{2 \times 6.6 \times 10^{h}}{8.314 \times 3.14 \times 2 \times 3} = \frac{2 \times 6.6 \times 10^2}{473.2} = \frac{1320}{413} = 2.8$$

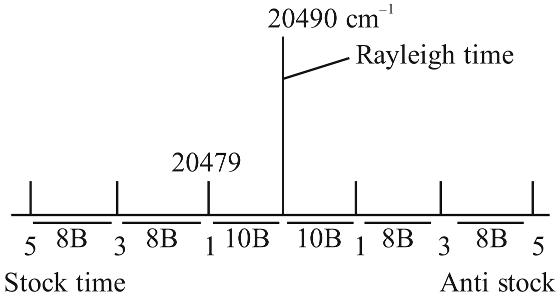
Correct option is (b)

GATE 2012

18. Intensity is proportional to the polarity of bond moe polar bond more intense

$\overset{\delta-}{O}-\overset{\delta+}{H}$ more polar

19. A 20491 cm^{-1} laser line was used to excite oxygen molecule because molecule made ^{16}O only because molecule have spin zero. In the spin zero molecule even J line are missing in Raman spectrum. e.g. O_2, CO_2.



Rotational constant B = 20491 – 20479 = 12

$10\ B = 12$

$B = 1.2\ cm^{-1}$

20. The next rotational stoke time is first stokes time in 20479

Second time difference is 8B

$B = 1.2$

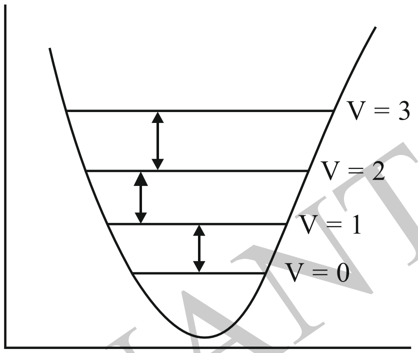
$8 \times 1.2 = 9.6$

So, second stock time is $20479 - 9.6 = 20469.7\ cm^{-1}$.

Correct option is (b)

GATE 2013

21. For harmonic oscillator every band gap is hν..



hν = 2885 cm–1.

Zero point energy of HCl molecule $\frac{1}{2}h\nu$

$\frac{1}{2} \times 2885\ cm^{-1}$

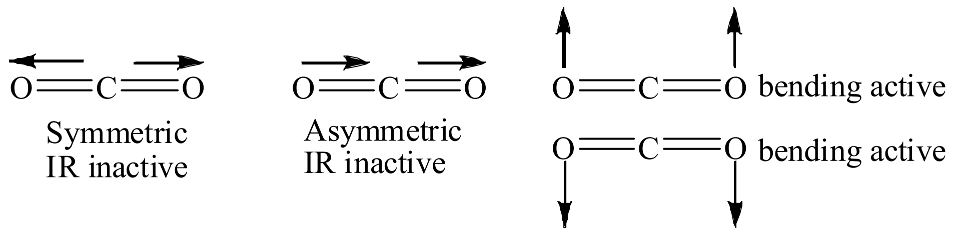
For joule, $\frac{1}{2} \times 2885 \times h \times c$

$$= \frac{1}{2} \times 2885 \times 6.6 \times 10^{-34} \times 3 \times 10^{10} = 2.8 \times 10^{-20}\ J$$

Correct option is (b)

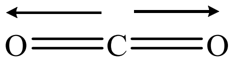
GATE 2014

22. Number of IR active vibrational normal modle of CO_2

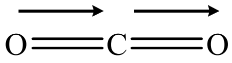


Correct option is (c)

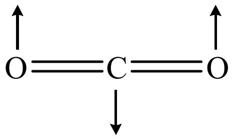
GATE 2016

23. (i)


Symmetric stretching IR-in active

(ii)


Asymmetric stretching IR-active

(iii)


Bending IR-active

Correct option are (ii) and (iii)

Correct option is (d)

GATE 2018

24. $E_{total} = BJ\,(J+1) + \left(\nu + \frac{1}{2}\right)\bar{w}_e - \left(\nu + \frac{1}{2}\right)^2 \bar{w}_e X_e$

$11493.6\ cm^{-1} = \left(3 + \frac{1}{2}\right)2998.3\ cm^{-1} - \left(3 + \frac{1}{2}\right)^2 + 2998.3 \times 0.124$

$11493.6\ cm^{-1}\ 9.716J\,(J+1)\ \frac{7}{2} \times 2998.3\ cm^{-1} - \frac{7 \times 7}{4} \times 2998.3 \times 0.0124$

$1454.99 = 9.716\ J\,(J+1)$

$J\,(J+1) = 149.7$

$J^{12} + J - 149.7 \Rightarrow J = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \Rightarrow J = 11.77 \approx 12$

Correct option is (12)

25. Spacing $\begin{cases} H^{35}Cl \rightarrow 2B \rightarrow 6.35 \times 10^{11}\ Hz \\ D^{35}Cl \rightarrow B \rightarrow ? \end{cases}$

$$B = \frac{h}{8\pi^2 I_C} \Rightarrow \frac{2B_{HCl}}{B_{DC}} = \frac{2\times\dfrac{h}{8\pi^2 I_{HCl}C}}{2\times\dfrac{h}{8\pi^2 I_{DCl}C}}$$

$$\frac{B_{HCl}}{B_{DCl}} = 2.14 \Rightarrow B_{DCl} = \frac{B_{HCl}}{2.14} \Rightarrow B_{DCl} = \frac{6.35\times10^{11}}{2.14} \Rightarrow B_{DCl} = 2.95\times10^{11}\text{ Hz}$$

GATE 2020

26Sol.: Given; change in quantum no. from

$J = 1$ to $J = 2$

So find, pure rotationa spectra of No molecule

We know that

$$B = \frac{h^2}{8\pi^2 I}\text{ in Joules}$$

in cm^{-1}

$$\frac{B}{\hbar c} = \frac{\hbar^2}{8\pi^2 I\hbar c} = \frac{\hbar}{8\pi^2 Ic}$$

and also

$$\frac{\Delta E_{1\to2}}{\hbar c} = \left[2(2+1)-1(1+1)\right]\frac{B}{\hbar c}$$

$$\frac{\Delta E_{1\to2}}{\hbar c} = \frac{4B}{\hbar c} = 681\text{ m}^{-1}\text{ or }6.81\text{ cm}^{-1}$$

Correct answer is 6.81 cm^{-1}

27Sol.: Given: No interaction between vibrational and rotational energy lavels in HF.

To find: frequency of R-branch line originating from J = 4, in its IR spectra.

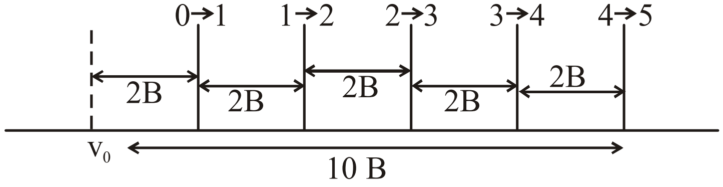
Also given

Rotational constant of nf = 19.35 cm^{-1}

$$\bar{v}_0 = 4138.52\text{ cm}^{-1}$$

We know that selection rule for R-pressur is $\Delta J = +1$

So



$$\therefore \quad v_{J=4\rightarrow 5} = v_0 + 10B$$

$$= 4138.5 + 10 \times 19.35$$

$$v_{J=4\rightarrow 5} = 4332.02\ \text{cm}^{-1}$$

GATE 2021

28Sol. $\nu = 2309\ \text{cm}^{-1}$

$$\nu\left(\text{cm}^{-1}\right) = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \quad (\text{k = face constant, } \mu = \text{reduced mass of HI molecule})$$

$$\mu = \frac{(127\times 1)10^{-3}\,\text{kg}}{128}\times\frac{1}{N_A}$$

$$\mu = \frac{127}{128}\times 1.66\times 10^{-27}\,\text{kg}$$

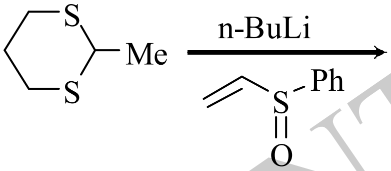
$$\overline{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

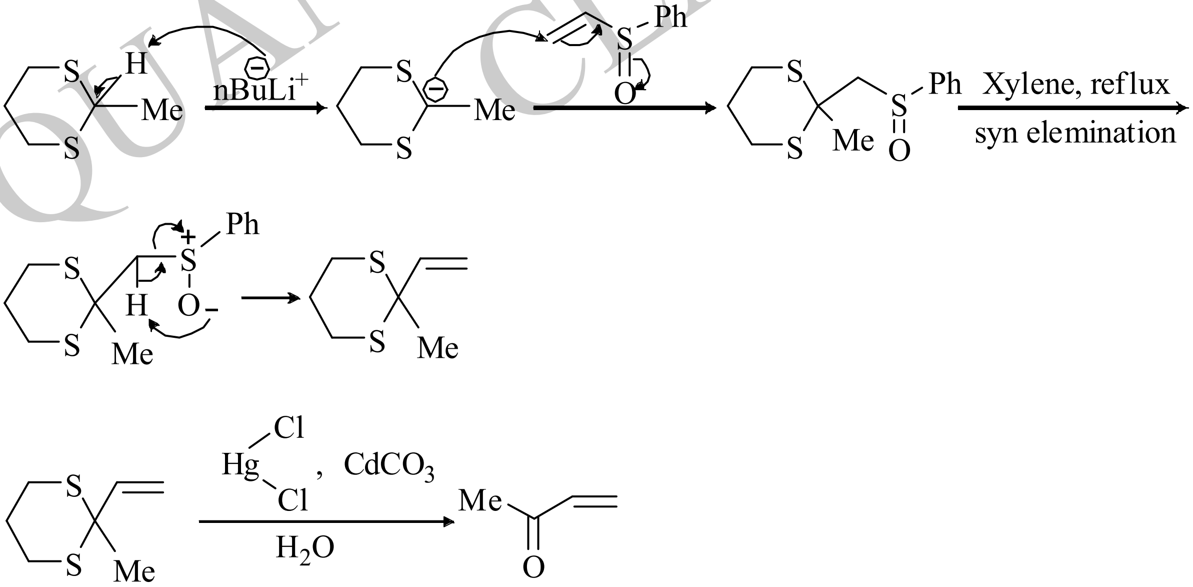
$$k = \left(2\pi c\times\overline{\nu}\right)^2\times\mu$$

$$= (2 \times 3.14 \times 3 \times 10^{10}\ \text{cm sc}^{-} \times 2309\ \text{cm}^{-1}) \times \frac{127}{128}\times 10^{-27}\times 1.66$$

$$= 311\ \text{Nm}^{-1}$$

29Sol.





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SOLUTION

GATE 2013

1. $q_{rot} = \frac{8\pi^2 IKT}{\sigma H^2}$ σ for homo = 2

$$= \frac{8\times3.14\times3.14\times7.5\times10^{-45}\times1.38\times10^{-23}\times500}{2\times6.6\times10^{-34}\times6.6\times10^{-34}}$$

$$= \frac{8\times3.14\times3.14\times7.5\times1.38\times10^{-23}}{2\times6.6\times6.6}\times10^{68}\times500 = \frac{816.37}{87} = \frac{4088185}{87} = 4691.7$$

Correct option is (4691.7)

GATE 2014

2. $\frac{\pi}{c} = \underset{\text{(shape)}}{BRT} + \frac{RT}{M}$

The slope of the plot increases with increase in temperature

Correct option is (a)

GATE 2015

3. For an ideal solution,

$\Delta_{min} G < 0$ $\Delta_{min} V = 0$

$\Delta_{min} S < 0$ $\Delta_{min} H = 0$

Correct option is (b)

4. $P_1 = 2.02 \times 10^3\ Nm^{-2}$; $P_2 = 1$ atm $= 1.01 \times 10^5$ Pa

$T_1 = 293K$; $T_2 = ?$

Applying Clausius Clapeyron equation

$$\ell n\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ell n\left(\frac{1.01\times10^5}{2.02\times10^3}\right) = \frac{-41000}{8.314}\left(\frac{1}{T_2} - \frac{1}{293}\right)$$

$$\ell n\ 50 = -4931.441\left(\frac{1}{T_2} - 0.0034129\right) \Rightarrow T_2 = 381.73\ K$$

Correct option is (382 to 385)

GATE 2019

5 Sol. $T_1 = 350$ K, $P_1 = 760$ torr

$T_2 = 300$ K, $P_2 = ?$

$\Delta H_{vap} = 30000\ J\ mol^{-1}$

Using Clayperon equation

$$\ln\frac{P_2}{P_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\Rightarrow \qquad \ln\frac{P_2}{760} = \frac{30000}{8.31}\left[\frac{300-350}{300\times 350}\right]$$

$P_2 = 136.32$ Torr

GATE 2020

6.Sol.: Given;

Icrution sucrose	Pure water
T = 30ºC	T = 30ºC
Vap. Press = 31.207 wittig	V.P. = 31.824 wittig
S = 1.1256 g/mol	activity coff = ?

To find: activity coff. of water in given for we know that

$$\text{activity coff} = \frac{\text{Observed colligative prop}}{\text{Calculated colligatie prop}}$$

Observed colligative prop (vapour press.) = 31.207 wittig and

Calculated colligative prop = $(1 - x)\ P_0$

Where x is mole fraction $= \left[\frac{n_1}{n_1 + n_2}\right]$

and P_0 is achiral vepour press. = 31.824 wittig

Now

$$x = \frac{n_1}{n_1 + n_2}$$

given that 1M, icrution of sucrose.

i.e. 1 mole in (aqueous) it so $n_1 = 1$ mole

and n_2 i.e. no. of moles of water

Also density $= \frac{\text{mass}}{\text{vol.}} = 1.1256 \text{ g / mol}$

i.e. 1 ml contains 1.1256g water

1000 ml contains 1125.6 g water

and molar mass of sucrose is 340.3 g/mol

So achiral weight of water in (1 mole g) polution is given as 1125.6 – 340.3 g.

Pressing values we get

$$= (1-x)P_0 \qquad \left(n_2 = \frac{1125.6-342.3}{10}\text{mol}\right)$$

$$= \left[1 - \frac{1}{1+\frac{1125.6-342}{18}}\right]31.824$$

Calculating this we get the answer as 1.003.

GATE 2021

7.Sol. Vapour pressure of toluene in 0.13 atm

Molar mass of toluene = 92 g /mol

Mole in 92 g of toluene $= \frac{92 \text{ g}}{92 \text{ g / mol}} = 1 \text{ mol}$

But the molar mass of hydrocarbon be xg/mol

Moles in 6g of hydrocarbon is $\frac{6}{x}$mol

Now $P^o_{\text{toluene}} = 0.13 \quad P_{\text{toluene}} = 0.12$

Relative covering V.P. = mole fraction of hydrogen carbon

$$\frac{P^o_{\text{toluene}} - P_{\text{toluene}}}{P^o_{\text{toluene}}} = \frac{\frac{6}{x}}{\frac{6}{x}+1}$$

$$\frac{0.13-0.12}{0.13} = \frac{6}{6+x}$$

$$\frac{0.01}{0.13} = \frac{6}{6+x}$$

= (0.01) (6 + x) = 6 (0.13)

0.06 + 0.01 x = 0.78

$0.01\ x = 0.78 - 0.06$

$$x = \frac{0.78 - 0.06}{0.01}$$

$x = 72\ \text{g/mol}$

8.Sol. $VP^{o}_{Hexane} = 0.198$ atm $VP^{o}_{Heptane} = 0.06$ atm

In section of 1L, 4 mole of hexane and 6 mole of Heptane (6M) are there.

$$\text{Mole fraction of hexane in vapour } (Y_A) = \frac{VP^{o}_{Hexane} \times \text{mole fraction of hexane in solution}}{P_{total}} \quad ...(1)$$

$$\text{Mole fraction of hexane in vapour } (Y_B) = \frac{VP^{o}_{Hexane} \times \text{mole fraction of heptone in solution}}{P_{total}} \quad ...(2)$$

Dwide (1) and (2)

$$= \frac{Y_A}{Y_B} = \frac{0.198 \times \frac{4}{10}}{0.06 \times \frac{6}{10}}$$

$$= \frac{Y_A}{Y_B} = 2.2$$

$Y_A = 2.2\ Y_B$

also $Y_A + Y_B = 1$

$2.2\ Y_B + Y_B = 1$

$3.2\ Y_B = 1$

$$Y_B = \frac{1}{3.2}$$

$= 0.3125$

$Y_A = 0.688 = (0.3125 \times 2.2)$

Correct option is (d)

9.Sol. $\lambda_{Rayleigh} = 532$ nm

$$\bar{\nu}_{Rayleigh} = \frac{1}{532 \times 10^{-7}}\ \text{cm}^{-1}$$

$$\bar{\nu}_R = 18796.99\ \text{cm}^{-1}$$

First stokes line $= \bar{\nu}_R - \bar{\nu}_F$

$= (18796.99 - 560)\ \text{cm}^{-1}$

$= 18237\ \text{cm}^{-1}$

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PHOTOCHEMISTRY

GATE 2005

1. $47\text{ppm} = 47\ \text{mgL}^{-1}$

$$\text{F.W} = 225 \Rightarrow n = \frac{47\times10^{-3}}{225} = 0.2088 \times 10^{-3} = 2.088 \times 10^{-4}\ \text{mol L}^{-1}$$

$$T = \frac{I}{I_0} = 0.297 \qquad \ell = 1.5\ \text{cm}$$

$$\log\left(\frac{I}{I_0}\right) = -\varepsilon CI$$

$$\log(0.297) = -\varepsilon \times 2.088 \times 10^{-4} \times 1.5$$

$$\varepsilon = 0.1693 \times 10^{4} \Rightarrow \varepsilon = 1.68 \times 10^{3}$$

Correct option is (c)

GATE 2015

2. $\%T = 39.8 \qquad C = 8 \times 10^{-5}\ \text{M}$

$\Rightarrow T = 0.398 \qquad \ell = 1\ \text{cm}$

$A = -\log T;\ A = \in Cl$

$$\in = \frac{A}{Cl} = \frac{0.4}{8\times10^{-5}\times1} = 0.05 \times 10^{5};\ \in = 5000$$

Correct option is (c)

GATE 2018

3. $$(E_x)_{460\ \text{nm}} = \frac{A}{c\ell} = \frac{0.144}{9\times10^{-3}\times1} = \frac{-144}{9\text{mM}-\text{cm}} \Bigg| (E_y)_{460\text{nm}} = \frac{-912}{12\text{mM}-\text{cm}}$$

$$(E_x)_{520\ \text{nm}} = \frac{0.765}{9\text{mM}-\text{cm}} \quad (E_y)_{520\ \text{nm}} = \frac{0.168}{12\text{mM}-\text{cm}}$$

$$\left.(A)_{\text{mix}}\right)_{460\text{nm}} = (E_x)_{460}\, c_x\ell + (E_y)_{460}\, c_y\ell$$

$$0.7 = \frac{0.144}{9\text{mM} - 1\text{cm}} \times c_x \times 1\text{ cm} + \frac{912}{12\text{mM} - 1\text{cm}} \times c_y \times 1\text{ cm}$$

$$0.7 = \frac{0.144}{9\text{mM}} c_x + \frac{0.168}{12\text{mM}} c_y \qquad ...(1)$$

Similarly from 520 nm data for mix

$$0.68 = \frac{0.765}{9\text{mM}} c_x + \frac{0.168}{12\text{mM}} c_y \qquad ...(2)$$

From equation (1) and (2),

$$c_y = \frac{\frac{0.765}{9\text{mM}} \times 0.7 - \frac{0.144}{9\text{mM}} \times 0.68}{\frac{0.765}{9\text{mM}} \times \frac{0.912}{12\text{mM}} - \frac{0.168}{12\text{mM}} \frac{0.144}{9\text{mM}}} = \frac{\frac{0.765 \times 0.7}{0.765 \times 0.193}}{12\text{mM}}$$

$$= 12\text{mM}\left\{\frac{0.765 \times 0.7 - 0.144 \times 0.68}{0.765 \times 0.912 - 0.168 \times 0.144}\right\} = 7.7967\text{mM}$$

GATE 2020

4.Sol.: $A = ECl$

$$A = \log\frac{1}{T}$$

$$A = \log\frac{1}{0.205}$$

$$\Rightarrow A = 0.69$$

$$C = \frac{0.69}{15000\text{ L mol}^{-1}\text{cm}^{-1} \times 1\text{cm}}$$

$C = 4.59 \times 10^{-5}$ mol/L

5.Sol.: Given → $\phi_f = 0.4$

$$z_f = 5 \times 10^{-9}\text{ s}$$

fluorescence decay constant $= \frac{\phi_f}{z_f} = \frac{0.4}{5 \times 10^{-9}\text{s}} = 8 \times 10^7\text{ s}^{-1}$

So, y = 8

GATE 2021

6. Sol. $\text{Power} = \frac{\text{Energy}}{\text{Time}}$

$E = \text{power} \times \text{time}$

$= 1 \times 10^{-6}$ watt $\times 1 \times 10^{-9}$ sec.

$E = 10^{-15}$ Joule

$$\text{Energy of a photon } = h\frac{c}{\lambda}$$

$$= \frac{6.626\times10^{-34}\times3\times10^{8}}{400\times10^{-9}\,\text{m}}\,\text{m / sec}$$

let the total photon he N

N × energy of single photon = Total energy emitued by comp (in a nano second)

$$= N\times\frac{6.626\times10^{-34}\times10^{8}\times3}{400\times10^{-9}} = 10^{-15}$$

$$N = \frac{10^{-15}\times400\times10^{-9}}{6.626\times10^{-34}\times3\times10^{8}}$$

$N = 20.12 \times 10^{2}$

$= 2012$

7. Sol. According Lambert – Beer law

Absorbance = E × C × l

E = absorptivity coefficient

C = concentration (molar)

L = path length

$A = 1710 \times 2 \times 10^{-3}\ \text{mol / L} \times 10^{-1}\ \text{cm}$

$= 3420 \times 10^{-4}$

$A = 0.3420$

$$\log\frac{I_0}{I} = 0.3420 \qquad \left[A = \log\left(\frac{I_0}{I}\right)\right]$$

$$\frac{I_0}{I} = 10^{0.3420}$$

$$\frac{I_0}{I} = 2.197$$

$I_0 = I \times 2.197$

Reduction in intensity $= I_0 - I$

$= I \times 2.197 - 1$

$= 1.97\ I$

$$\%\ \text{reduction} = \frac{1.197\,I}{I}\times100$$

$$= \frac{1.197\ I}{2.197\ I}\times100$$

$= 54.4\ \%$

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GASES

GATE 2006

1. According to kinetic theory, the gas particles have same mass but negligible volume compared to volume of gas.
   Correct option is (a)
2. Fugacity cannot be zero for gas
   Correct option is (a)
3. One mole each of H_2CO_3, $NaHCO_3$ and Na2O$_3$ are added to water to prepare one litre solution. The pH of the solution is (Hint: $pK_{a_1} = 6.4$ and $pK_{a_2} = 10.3$)

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2}$$

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{6.4 \times 10.3}{2} = 8.31$$

   Correct option is (b)
4. Molality = 2m, for water $k_b = 0.512$
   $\Delta T_b = kbm$
   $\Delta T_b = 0.512 \times 2 = 1.024 \Rightarrow$ $T_b - T_b^* = 1.024$
   $T_b = 101.024°C$
   Correct option is (b)

GATE 2008

5. $$\lambda = \frac{1}{\sqrt{2}\ nd^2} = \frac{1}{\sqrt{2} \times 1 \times 10^{-20}} = \frac{10^{20}}{\sqrt{2}} \approx 10^{19}$$

   Correct option is (b)

GATE 2011

6. Kinetic gas equation, $PV = \frac{1}{3} mN_A.u^2$

$$PV = \frac{1}{3} mN_A u^2 \times \frac{2}{2} = \frac{2}{3} N_A \frac{1}{2} mu^2 = \frac{2}{3} N_A \overline{E}$$

$$\left(P = \frac{2}{3V}\bar{E}N_A\right)$$

Correct option is (c)

GATE 2013

7. $V_{total} = 4L$

$n_{H_2} = \frac{2}{2} = 1$ mol $\qquad n_{CO_2} = \frac{176}{44} = 4$ mol

$n_{total} = 5$ mol $\qquad T = 300K$

$$P_{total} \cdot V_{total} = n_{total}RT$$

$$P_{total} = \frac{5\times 0.0831\times 300}{4} = 31.1625$$

$$PP_{H_2} = x_{H_2}\ P_{total} = \frac{1}{5}\times 31.1625 = 6.2325 \text{ bar}$$

Correct option is (6.2325)

GATE 2014

8. $$v_{avg} = \sqrt{\frac{8RT}{\pi M}} \Rightarrow \frac{v_{H_2}}{v_{He}} = \frac{\sqrt{\frac{1}{2}}}{\sqrt{\frac{1}{4}}} \Rightarrow \frac{v_{H_2}}{V_{He}} = \sqrt{\frac{4}{2}}$$

$$\Rightarrow \frac{v_{H_2}}{v_{He}} = \frac{\sqrt{2}}{1} \Rightarrow \frac{v_{H_2}}{v_{He}} = 1.414$$

Correct option is (1.4 to 1.5)

QUANTA CHEMISTRY CLASSES
An institute of Chemical Sciences

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ANALYTICAL

GATE 2005

1. Current efficiency is not related to polarography

   Correct option is (d).

2. n = 2 : $M^{2+} + 2e^{-} \rightarrow M$

   $I_d = 7.5\mu A$

   $E = 0.615;\ I = 1.5\ \mu A \Rightarrow E = E_{1/2} - \frac{0.0591}{n}\log\frac{[M]}{[M^{2+}]}$

   $E = E_{1/2} - \frac{0.0591}{2}\log\frac{I}{I_d - I} \Rightarrow -0.615 = E_{1/2} - \frac{0.0591}{2}\log\frac{1.5}{7.5-1.5}$

   $\Rightarrow -0.615 = E_{1/2} + 0.01779 \Rightarrow E_{1/2} = -0.63270$

   Correct option is (d)

3. (*)

GATE 2007

4. (*)

GATE 2012

5. Mole of Ca^{+} will be

   Molarity of Na_2EDTA × volume of Na_2EDTA

   $= 0.001 \times 2mL = 0.001 \times \frac{2L}{1000} = 2 \times 10^{-6}$ mol

   Now, 2×10^{-6} mol of $Ca^{2+} = \left(\frac{1\ \text{mol CaCO}_3}{1\ \text{mol Ca}^{2+}}\right)\left(\frac{100\text{g of CaCO}_3}{1\ \text{mol CaCO}_3}\right) \times 2 \times 10^{-6}$ g of $CaCO_3$

   $= 2 \times 10^{-4}$ g of $CaCO_3$

   Thus, concentration of $CaCO_3 = \frac{2\times10^{-4}\text{g}}{\text{volume}} = \frac{2\times10^{-4}}{10\ \text{mL}} = 2 \times 10^{-5}$ g/mL

   Correct option is (d)

QUANTA CHEMISTRY CLASSES
An institute of Chemical Sciences

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LIQUID SOLUTION

GATE 2007

1. Sol : (*)

GATE 2011

2. Depression in freezing point

$\Delta T_f = i.k_f.x$

Glucose is non electrolyte i = 1

$k_f = 1.86k\ (mol/kg)^{-1}$

$$\text{Molality (m)} = \frac{\text{moles of solute}}{\text{mass of solvent in kg}} = \frac{0.01}{1} = 0.01$$

$\Delta T_f = 1 \times 1.86 \times 0.01 = 0.0186$

$T_f = 0 - 0.0186 = -0.0186$

Correct option is (d)

3. At NTP concentration of water = 55.5 mol/L

$\pi = CRT$

$$\frac{\pi_i}{\underset{\text{at || bar and 298K}}{C_1RT_1}} = \frac{\pi_2}{\underset{\text{(AT NTP)}}{C_2RT_2}};\ \frac{11}{C_1 \times 298} = \frac{1}{55m \times 273} \Rightarrow C_1 = 559.28$$

$$a_w = \frac{C_1}{C_2} = \frac{559.28}{55.5} = 10.07 = \frac{10.07 + 100}{1000} = 1.00\%$$

Correct option is (a)

GATE 2012

14. $$-\ell n(x_A)_c = \frac{DH_{f \cdot A}}{R}\left[\frac{1}{T_e} - \frac{1}{T_{m,A}}\right]; -\partial n(x_B)_c = \frac{DH_{f.B}}{R}\left[\frac{1}{T_e} - \frac{1}{T_{m,B}}\right]$$

$$In(x_A) = -\frac{DH_{f \cdot A}}{R}\left[\frac{1}{T_e} - \frac{1}{T_{m,A}}\right]$$

$$x_A = e^{-\frac{DH_{f.A}}{R}\left[\frac{1}{T_e}-\frac{1}{T_{m,A}}\right]} \Rightarrow \left\{1-x_B = e^{-\frac{DH_{f.A}}{R}\left[\frac{1}{T_e}-\frac{1}{T_{m,A}}\right]}\right\} \Rightarrow 1-x_B - e^{\left[-\frac{\Delta Hfu(A)}{R}\left[\frac{1}{T_e}-\frac{1}{T_{m,A}}\right]\right]}$$

correct option is (d)